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SYNTHESIS OF NOVEL SILOXANE CONTAINING BLOCK COPOLYMERS FOR IMPACT MODIFICATION OF POLYBUTYLENETEREPHTHALATE

by

Ian Walker

A thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Sponsoring Establishment : Department of Applied Physics
Sheffield City Polytechnic

Collaborating Establishment : AKZO Corporate Research

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To my Mum and Dad

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The aim of this work was to synthesise poly(butylene terephthalate) (PBT) poly (dimethylsiloxane) (PDMS) block copolymers, containing the hydrolytically stable Si-C linkage. A number of routes involving mutually reactive oligomers were studied. Once synthesised the effect of the copolymer as a toughening agent for the PBT matrix was investigated.

Siloxane copolymer precursors were synthesised by an equilibration reaction. The relative molar mass (RMM) of the precursor was governed by the initial ratio of end blocker to cyclic species. The functionality of the precursor determined by the end blocker. α, ω hydroxy PBT oligomeric precursors were chemically modified, if necessary, to form mutually reactive species.

Initial block copolymer synthetic routes concentrated on chloroplatinic acid catalysed hydrosilations in solution. This involved α, ω di(hydrosilane) PDMS and α, ω divinyl functionalised PBT. The lack of a suitable common solvent together with competing side reactions limited the progress of this route. Melt hydrosilation reactions proved ineffective also, because of the thermal instability of the catalyst.

Further block copolymer experiments involving mutually reactive oligomers were performed in the melt. The most promising of these was one of transesterification. This used α, ω hydroxypropyl PDMS (RMM 1000) and α, ω hydroxy PBT (RMM 2000) precursors. Analysis indicated successful reaction to form a copolymer of low RMM. A higher RMM copolymer was desirable, for improved mechanical properties, and a number of approaches to achieve this were followed. Problems of competing reactions and ineffective catalysis were encountered. However, a material with promising mechanical properties was formed when using a diisocyanate as a chain extender.

A PBT-PDMS copolymer was blended by itself, and also together with high RMM PDMS, in the PBT matrix. The mechanical properties of the blends were studied and compared. An improvement in impact properties, as compared to PBT, was achieved when the copolymer was used as an emulsifying agent in a PBT-PDMS blend.

1. INTRODUCTION

A large number of thermoplastic polymers exhibit severe limitations in their end use when toughness and high impact resistance are required (1,2). Engineering thermoplastic polyesters, such as poly(butylene terephthalate) (PBT)and poly(ethylene terephthalate), are no exception to the rule. Since PBT was first produced commercially for use as a high performance polymer by Celanese in 1968 (3), it has become a very important material for many injection moulding applications (4). Some typical examples include fuse boxes, oven handles and control switches, headlamp housings, friction bearings and castors. The success which PBT has achieved in the market place is attributable to the combination of such properties as chemical resistance, good tensile and flexural moduli, a maximum service temperature of approximately 140^{o}C, high mould deflection temperatures, good electrical insulation and sliding friction behaviour as well as short cycle times in injection moulding. Many of these desirable properties are derived from the high degree of crystallinity of PBT. However, this high degree of crystallinity is also responsible for the relatively low impact resistance. The lack of toughness in turn excludes PBT from some very important applications, such as automobile body panels, where toughness and high impact resistance are required.

These shortcomings may be overcome by blending PBT with a suitable rubbery component (5 - 10). The enhancement of the toughness obtained is due to the presence of finely dispersed rubber particles throughout the matrix. The elastomeric phase must be in the rubbery state in the service temperature range of the thermoplastic if it is to be effective. One route to toughening a matrix is to incorporate a block copolymer consisting of both the host material and the rubber, in this way it is hoped to gain toughening together with good interfacial adhesion between the rubber and the matrix.

Block copolymers are generally characterized by long sequences (segment lengths dependent on copolymer system) of each of two dissimilar structures chemically combined at their terminal segments. They represent an interesting class of materials whose unique molecular architecture can lead to useful product properties (11, 12). There are three distinct architectures within this class of polymer. The structures may be A - B diblock copolymers (Fig.1.1), A - B - A triblock copolymers (Fig.1.2) and $\leftarrow$ A - B $\rightarrow_n$ multiblock copolymers (Fig. 1.3) where A and B denote chemically different chain components.

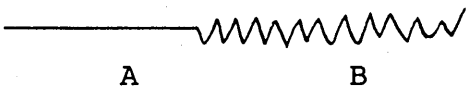


Fig. 1.1 A diblock copolymer or AB copolymer

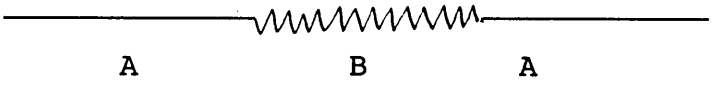


Fig. 1.2 A triblock or A - B - A copolymer

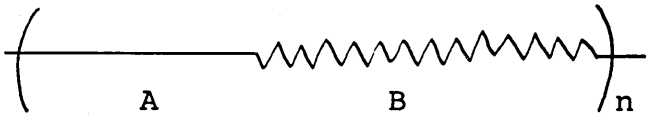


Fig. 1.3 A multiblock or $(A - B)_n$ copolymer

where n = 2,3,4.....

The $\text{-}(\text{-A-B-})_n$ architectural type can be subdivided into two further types i.e. alternating and random block copolymers shown below (Figs. 1.41 and 1.42).

A B A B A B A B A B A B Fig.1.41 Alternating

A B B B A A B A B B A A Fig.1.42 Random

A requirement for rubber toughening is that the two components should be incompatible such that a two-phase structure exists. Stehling et al (13) showed that the Hildebrand solubility parameters of the two materials must differ by at least 0.4 $(MJm^{-3})^{1/2}$ to give a two phase structure. If the physical properties of the A and B blocks differ sufficiently and the block segments are of sufficient length (14 - 16) , e.g.polysulphone /poly(dimethylsiloxane) (PDMS) 5000/5000 RMM, these

polymers will tend to phase separate on a microscopic scale. Thus small domains of one type of the block tend to be dispersed in the matrix material.

The chemical bond linking the block structures prevents them from separating on a macroscopic scale characteristic of incompatible physical blends. Generally, simple physical blends of an elastomer with a thermoplastic give rise to an unfavourable free energy of mixing. This results in the formation of an incompatible blend that is deficient in many key mechanical properties, due to the poor adhesion at the interface between the two phases. Therefore, strong adhesion between the matrix and the dispersed phase is important in preventing the exclusion of the rubber phase and hence the formation of a useful rubber modified thermoplastic.

Especially interesting block copolymers are combinations of rubbery and thermoplastic polymers, which constitute a family of materials known as thermoplastic elastomers, e.g. styrene/isoprene/styrene (Kraton) and polyether / polyester (Hytrel, Arnitel) (17). The properties of these materials depend not only on the polymers chosen but also on their respective sequence lengths and ability to form discrete rubbery and glassy domains. Generally though these materials are charactierised by the mechanical properties of a crosslinked rubber together with the processibility of a thermoplastic. These polymers are normally of either A - B - A or $-\!\!\left(A - B\right)_n$ architecture wherein A is a high Tg

thermoplastic and B is a very low Tg rubber i.e. Tg well below room temperature e.g. poly(oxytetramethylene) Tg ~ -80°C. Such a combination can yield a material with a very broad service temperature range.

The degree of toughening is also affected by the size of the rubber particles, the typical range being between 0.1 and 5.0 μm. However, before discussing the optimum particle size one must consider the toughening mechanisms involved. A variety of quite different mechanisms for rubber toughening have been proposed, ranging from absorption of energy by the deforming rubber particles in front of the crack tips to the enhancement of microcracking at the particles (18 - 22). It is generally now accepted however that the profuse generation of crazes and/or shear bands from rubber particles is of major importance for toughening in these systems, (1, 23 - 28).

When the deformation is restrained in two dimensions, because the thickness and width of the specimen are small, the deformation is said to take place in plane strain. If the deformation occurs at constant volume or is due to a compressive stress and the material is isotropic, then the shear deformation of a band will occur at an angle of about 45° to the direction of applied stress. This is known as a shear band and one is shown emanating from a notch in Fig.1.5.

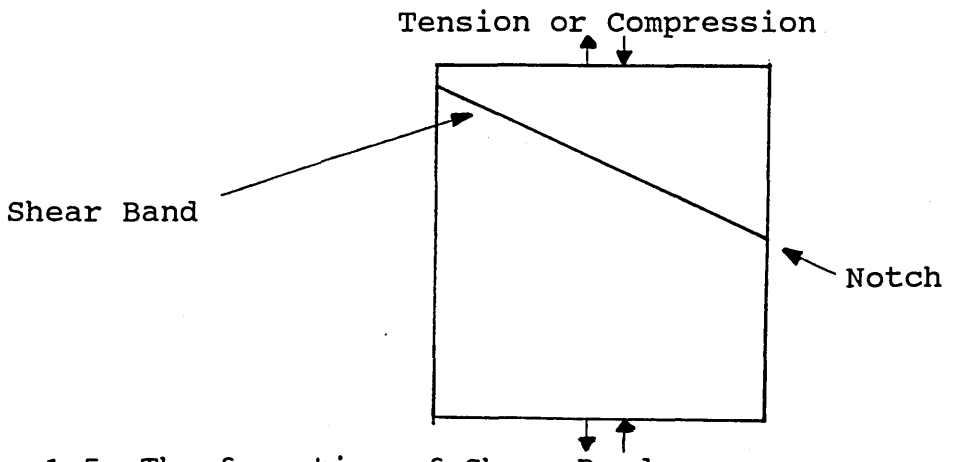


Fig.1.5. The formation of Shear Bands

In tensile experiments some materials deform by crazing as shown in Fig.1.6. The applied tensile stress causes microvoids to nucleate at points of high stress concentration. These can be due to scratches, flaws or cracks in the material. In multiphase materials, the interface between the dispersed phase and the matrix may act as a stress concentrator. Unlike shear bands, crazing develops at right angles to the applied tensile stress. Initially the crazes do not amalgamate to form a true crack. The reason for this is that fibrils of orientated material cross the craze and enable a transfer of stress across it. A crack develops only when the fibrillar material is broken down.

Crazing is often a precursor to brittle fracture and is highly localised. A volume increase accompanies craze formation, unlike the formation of shear bands. Much energy is absorbed in the formation of crazes and in breaking down the fibrils. If many crazes are formed the

failure may be ductile rather than brittle. Here lies the key to increasing fracture toughness.

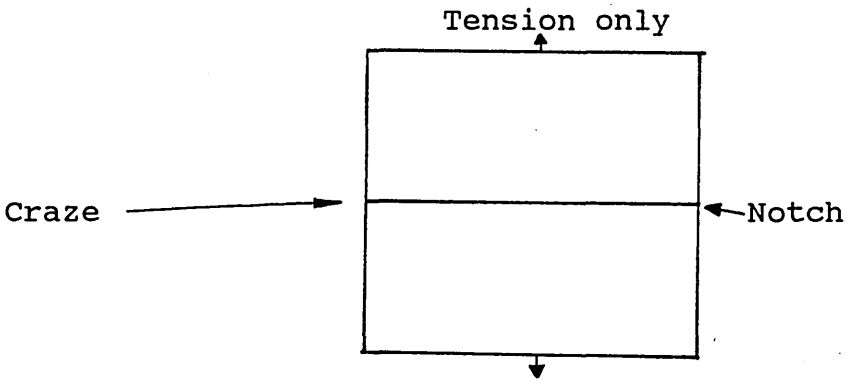


Fig. 1.6. Formation of crazes

In both types of failure (shear yielding and crazing) a more ductile behaviour can be obtained if the two mechanisms are not localised, since a greater amount of energy can be absorbed in forming numerous crazes or shear bands. If a dispersed elastomeric phase of particles of the correct diameter is incorporated into a brittle matrix, the particles act as numerous stress concentrators. These encourage either shear band formation or crazing, whichever is the preferred failure mode for the material, and this leads to a large energy absorption accompanied by ductile behaviour.

In some materials under experimental conditions shear band formation and crazing may occur simultaneously. As a general rule, the mechanism which is dominant in the toughened polymer will simply reflect the main mechanism which is operative in the unmodified matrix. Thus in high impact polystryrene (HIPS), crazing is usually the dominant

mechanism whilst shear yielding is generally the major mechanism in rubber toughened PVC. However, microstructural features of the toughened polymer, such as particle size, will affect the balance of the mechanisms, as will the rate and temperature of test. Thus incorporation of a dispersed rubber phase may give toughening due to :-

(i) multiple crazing

(ii) shear yielding, accompanied by cavitation of of rubber particles

(iii) or in some cases both mechanisms.

Some consensus has now been reached that the optimum particle size of the rubber (18, 29 - 32), depends on the mechanism of fracture. Thus where failure occurs through craze formation, this optimum rubber particle size is higher than when a shear yielding mechanism is operative. Block copolymers are often used in toughening since they offer a better degree of morphological control. For example, when compared with a similar copolymer a polystryene / polyisoprene graft copolymer showed a much more diffuse interfacial region and some suggestion of polyisoprene inclusion within the polystryene phases (33). The observations indicated additional constraints to phase separation in the graft copolymer assigned to the non-uniform distribution of the side chains along the backbone.

The aim of this research has been to synthesise and characterise block copolymers of PBT (Tg ~ 50°C) and PDMS (Tg ~ - 120°C). The copolymer was then dispersed throughout the PBT matrix in an attempt to form a toughened PBT system.

2. LITERATURE REVIEW

2.1 Siloxanes

The first syntheses of major types of polyalkylsiloxanes were performed by Friedel, Ladenburg and Crafts in 1865 - 1871 (34 - 36). Ladenburg probably obtained the first alkylsiloxane polymer by saponification of either diethyldichlorosilane or diethyldiethoxysilane. The structure of these polysiloxane products were mistakenly assumed to be similar to ketones.

$$(C_2H_5) - \underset{\underset{O}{\|}}{Si} - (C_2H_5)$$

The first pure cyclic siloxane, hexaphenyl cyclotrisiloxane, was prepared and characterised in the early 1900's by Dilthey (37).

Although siloxane polymers were first prepared by Ladenburg, it was not until the early 1900's that the siloxane polymeric structure was proved by F.S. Kipping et al (38). Kipping prepared a large number of linear and cyclic polymers of the type $(R_2Si\ O)_n$ and $HO(R_2SiO)_n\ H$ and also crosslinked $(R\ Si\ O_{3-n}\ H_{3-2n})_m$. Kipping's studies disclosed for the first time that the Si - O - Si group differed dramatically from the C - O - C group in its reactivity and that the Si - O - Si group could be particularly easily cleaved by acids, Lewis acids or Lewis bases. Furthermore, he was first to observe the catalytic effect of acids and bases for the now commercially

important siloxane redistribution and ring opening polymerisations (39, 40). Following this period, commercial production of siloxane polymers was hindered by the absence of convenient methods for monomer synthesis. In the 1930's Rochow at General Electric (37, 41) and Muller in Germany (nine months later) independently discovered what is known as the "Direct Process"(42) and in so doing, pioneered an industry via the economical manufacture of the family of methylchlorosilanes necessary for siloxane production. Controlled hydrolysis of the various organohalosilanes then provided the cyclic trimers and tetramers used for polymerisation.

2.11 Properties

Polyorganosiloxanes are characterised by combinations of chemical, mechanical and electrical properties not common to any other class of polymer. They are amongst the most commercially important of the inorganic backbone polymers and their properties have led to many uses. Example applications are presented in Table 2.1.

A valuable property of the siloxanes is their thermal stability, accompanied by an unusually small dependence of physical properties on temperature as compared to organic rubbers. For example, general purpose silicone rubber compounds reportedly (45) perform at temperatures ranging from -100 to 260^{o}C without undergoing physical property deterioration. Stability at high temperatures probably results mainly from the high bond

TABLE 2.1 Practical Uses of Silicones,General Product Types and Example Application Areas (43, 44).

Fluid Application

Plastic Additives	Greases
Hydraulic Fluids	Particle and Fibre Treatments
Release Agents	Cosmetic / Health Product Additives
Antifoamers	Polishes
Water Repellency	Lubricants
Surfactants	

Resin Applications

Varnishes	Electrical Insulation
Paints	Pressure Sensitive Adhesives
Moulding Compounds	Laminates
Protective Coatings	Release Coatings
Encapsulants	Adhesives

RTV Rubber Applications

Sealants	Encapsulants
Adhesives	Electrical Insulation
Gaskets	Glazing
Foams	Medical Implants
Moulding Parts	Surgical Aids
	Mould Making

Heat-Cured Rubber Applications

Tubing and Hoses	Auto-ignition Cable and
Belting	Spark Plug Caps
Wire-Cable Insulation	Medical Implants
Surgical Aids	Laminates
Fuel Resistant Rubber Parts	Fabric Coating
Penetration Seals	Electrically Conducting Rubber

energies of Si - O bonds (see Table 2.2).

TABLE 2.2 Comparative Bond Energies (41)

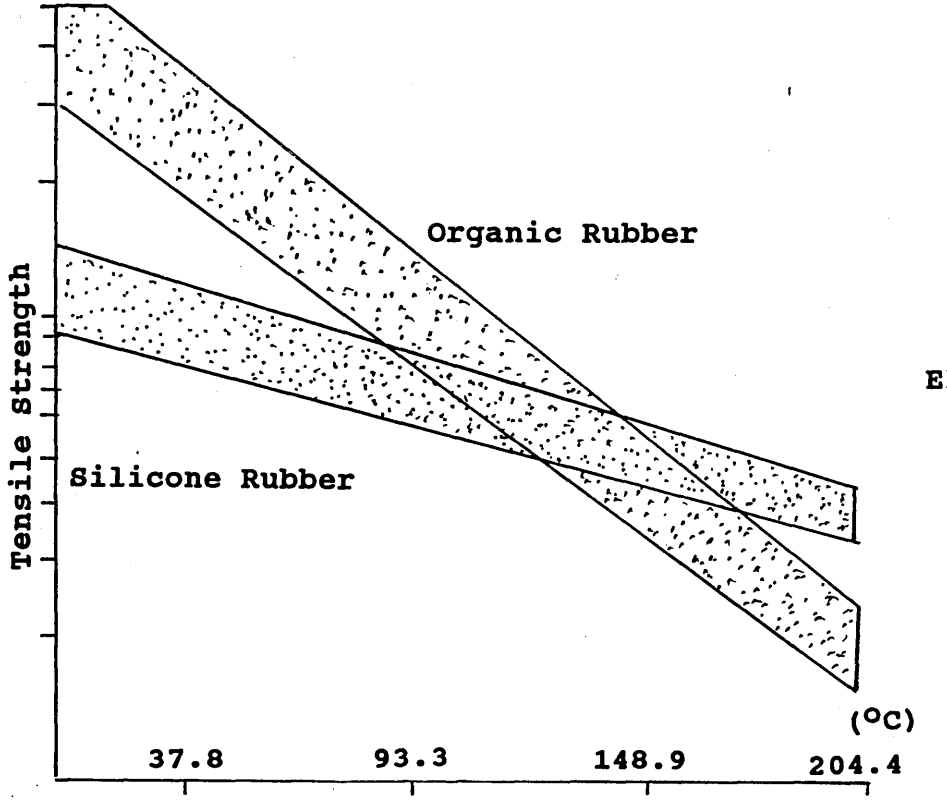
SINGLE BOND	ENERGIES (KCAL/MOLE)
Si - O	88.2, 106, 117, 101
C - O	84.0, 80.9
Si - C	69.3, 75.0, 64, 52 - 76
C - C	83.1, 84.9

These bond energies reflect both the polar nature of the Si - O bond together with additional interactions between the atoms. One of these is backbonding between the filled p orbitals of oxygen and the empty $3d_z^2$ and $3d_{x^2-y^2}$ orbitals of silicon (46, 47)). Additionally it has also been suggested that hyperconjugation effects involving σ orbitals would also explain the physical properties observed (48). Intramolecular dipole stabilisation, which also probably contributes to the thermal stability, is offered by a possible spiral conformation which has been proposed for polyorganosiloxane molecules (37). In such a conformation the siloxane bonds are orientated towards the screw axis with the organic substituents arranged to form a non-polar sheath around the molecule. Flory et al (49) attributed this helical shape to the intramolecular dipole stabilisation offered through the positioning of an Si - O bond opposite an O - Si group in immediately adjacent turns of the helix (and vice versa). This helical structure also helps to explain the unusually low intermolecular forces existing in siloxanes. It is these weak intermolecular forces that are mainly responsible for the wide low

temperature application range of polydimethylsiloxane elastomers.

High relative molar mass polydimethylsiloxane rubbers have a glass transition temperature of -123°C and crystallise at a rapid rate at approximately -54°C (37). Although rotation of the Si - O bond is restricted to a certain degree, the siloxane backbone is considerably more flexible than that of most other polymers (49). Methyl groups reportedly rotate around the Si - O bonds with unusual ease, therby forcing the siloxane molecules further apart. Undoubtedly, the larger size of silicon as opposed to carbon and the large oxygen bond angle (143°) contribute to the wide separation of the substituent organic groups , thereby enhancing free rotation about backbone bonds. Flexibility of the siloxane chain decreases with increased steric interaction between substituents. Replacement of the methyl groups by phenyl groups induces a particularly marked effect (50, 51).

As with most organic rubbers, unfilled polydimethylsiloxanes have poor mechanical properties around room temperature and below (37, 41). However, compared to organic rubbers siloxane polymers show a substantially smaller decrease in mechanical properties as the temperature is raised (see Fig.2.1, Silicone rubber vs Organic rubber (45)).



Variation Of Tensile Strength With Temperature

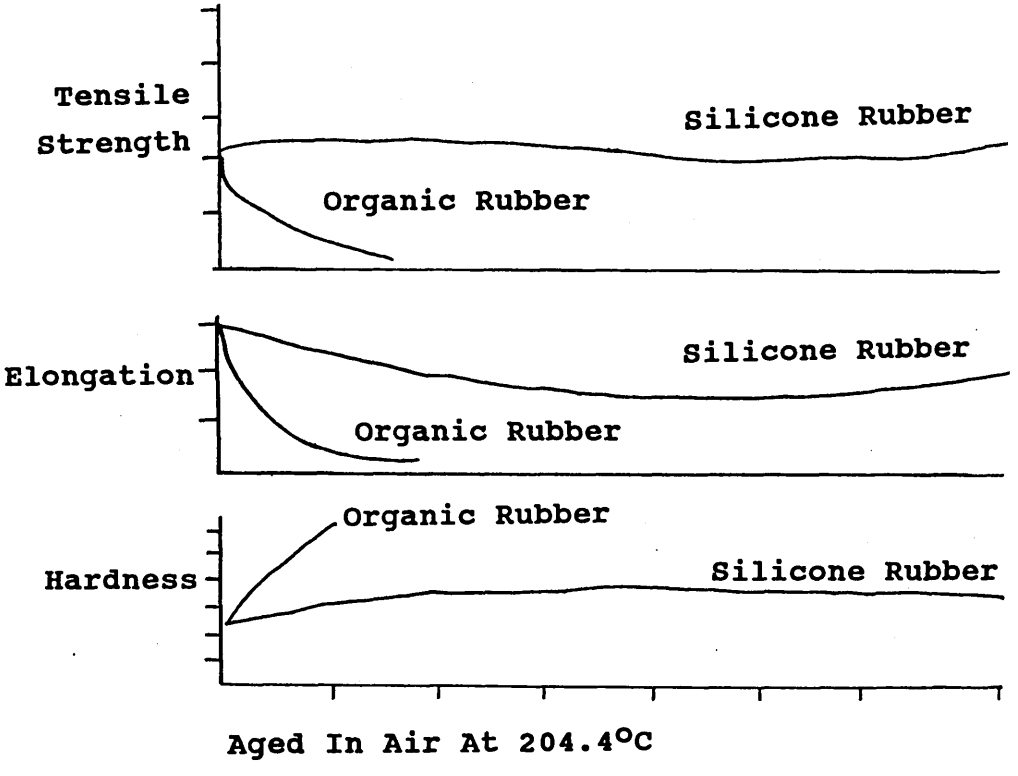


Figure 2.1 Silicone Rubber vs Organic Rubber (45)

The viscosities of low molar mass linear and cyclic polydimethylsiloxanes are lower than that of hydrocarbons of comparable relative molar mass (RMM). The temperature coefficient of viscosity is also extremely low. The poor mechanical properties and low viscosity result from the weak intermolecular forces in siloxane molecules. With increases in temperature the tendency of the siloxane backbone to adopt helical conformations is reduced. This leads to a strengthening of intermolecular forces and consequently more chain entanglements. Hence to higher viscosities and improved mechanical properties. This conformation effect compensates for the expected effects of increasing temperature, and can be used to explain why many of the physical properties of siloxanes remain relatively unaffected by increasing temperature.

A further important property of siloxanes, which is also due to the weak intermolecular forces, is their relatively low surface free energies. A high molar mass silicone oil has a surface tension of only 22 dynes cm^{-1} (37), which is characteristic of a completely organic surface. This renders siloxanes useful as additives for applications wherein high surface activity or great spreading power is necessary. The methyl siloxanes are highly hydrophobic and their low surface tension coupled with their insolubility in water enables them to act as antifoams with aqueous systems. However in certain organic foams in which the siloxane is soluble, their inherent surface activity often

promotes foaming (52). They also aid the flow of paints and varnishes and act as mould release agents.

Due to the polarity of the siloxane bond, these materials are resistant to homolytic cleavage. This, together with the fact that these molecules contain no double bonds renders them moderately resistant to oxidative degradation.

Siloxanes are susceptible to effects of high energy radiation and γ- radiation has been used to produce crosslinked networks or rubbers (53). The susceptibility of siloxanes to the effects of radiation is governed to a large extent by the nature of the organic substituent groups present on silicon. Polymers containing methyl, vinyl, hydrogen or trifluoro propyl groups are relatively easily affected by radiation, whereas those containing phenyl or other aromatic groups show improved radiation resistance.

Many other interesting and useful properties are exhibited by these materials such as high gas permeablities, excellent electrical properties with high resistivity and low dielectric loss. They also have high resistance to ultraviolet radiation, ozone and corona discharge.

2.2 Preparation of Siloxanes

2.21 Monomer Synthesis

The first step toward the production of siloxane polymers is the conversion of elemental silicon to silanes which are subsequently hydrolyzed to form cyclic and linear siloxane oligomers. By far the most important reaction used industrially is Rochow's "Direct Process" (54). This involves the preparation of dialkyl - and diaryl - dichlorosilanes without the use of classical substitution methods involving magnesium, sodium , zinc or mercury. The direct process utilises the action of hydrocarbon chlorides (or bromides) on elemental silicon to produce a mixture of alkyl or aryl halosilanes of the type R_A Si X_B where A + B = 4. Copper is employed as a catalyst and the reaction takes place at ca 550K. The reaction may be summarised as:

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

$$2\,CH_3Cl + Si \xrightarrow[Cu,550K]{} (CH_3)_2\,Si\,Cl_2$$

Reaction Scheme 2.1 The "Direct Process"

Small amounts (~ 15 - 20 %) of methyltrichlorosilane and trimethylchlorosilane are also produced. Reactions of the following types [Reaction scheme 2.2 (a - d)] occur during the direct process and a complex mixture of products results.

$$2RX + Si \longrightarrow R_2Si\,X_2 \qquad (a)$$

$$3RX + Si \longrightarrow R\,Si\,X_3 + 2R\cdot \qquad (b)$$

$$3RX + Si \longrightarrow R_3Si\,X + X_2 \qquad (c)$$

$$2X_2 + Si \longrightarrow Si\,X_4 \qquad (d)$$

Reaction Scheme 2.2. Reactions during "Direct Process"

Various organohalosilanes, tetraalkylsilanes, organo - H - halosilanes, silicon tetrachloride and small amounts of hydrocarbons (generated through the combination of two alkyl radicals) are produced. Organic free radicals produced as shown in Reaction 2.2 (b) are also responsible for the formation of hydride substituted silanes. A certain amount of control over the composition of the product mixture can be achieved by altering such parameters as catalysts, temperature and use of diluent gases. A typical industrial product mixture is shown in Table 2.3.

TABLE 2.3 Typical Yields of Chlorosilanes from the Direct Reaction

Compound	%	Bpt/^{o}C
$(CH_3)_2Si\,Cl_2$	75	70
$CH_3Si\,Cl_3$	10	66
$(CH_3)_3Si\,Cl$	4	58
$CH_3Si\,H\,Cl_2$	6	41
$Si\,Cl_4$ $(CH_3)_4Si$ $H\,Si\,Cl_3$ Disilanes	5	58 26 32

Dimethyldichlorosilane is purified by distillation. The proportion of dimethyldichlorosilane obtained from the direct process can be increased by a redistribution reaction using aluminium chloride as the catalyst.

$$(CH_3)\,Si\,Cl_3 + (CH_3)_3\,Si\,Cl \xrightarrow[420\ K]{AlCl_3} 2(CH_3)_2\,Si\,Cl_2$$

2.22 Polymer Synthesis

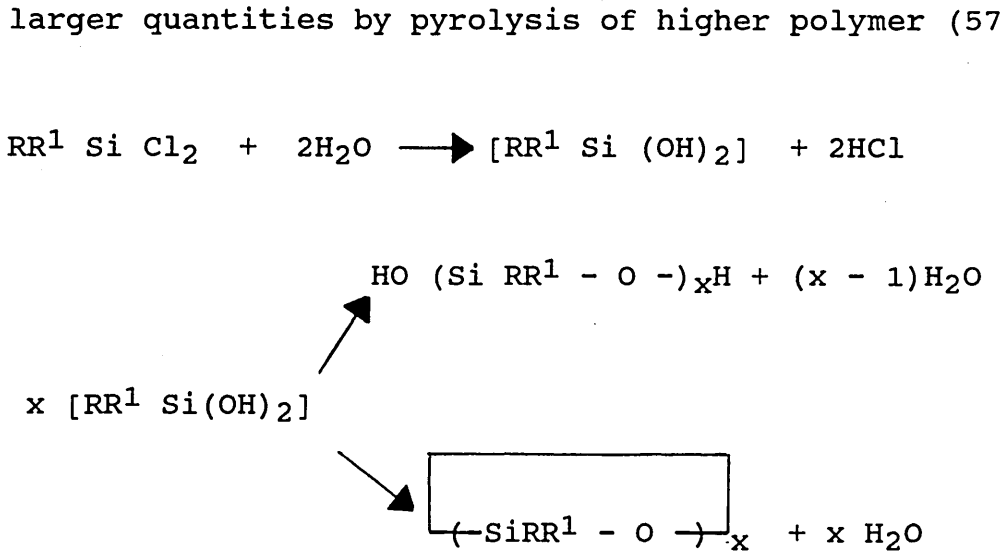
For polysiloxane production there are a number of options available (39, 40, 55). These include:

1. Hydrolytic processes based mainly on hydrolysis of organohalosilanes produced in the direct process, or organoalkoxysilanes.
2. Redistribution reactions involved in the anionic or cationic polymerisation of cyclic monomers and low molar mass linear species.
3. Non-hydrolytic processes based on reactions of organohalosilanes or organoalkoxysilanes with alcohols or acids.
4. Anionic polymerisation of hexamethylcyclotrisiloxane (D_3) using Li^+ as the counterion.
5. Thermal polymerisation.

Of these processes only (1) and (2) are of commercial importance. However, as (2) has been mainly used in this research programme the following discussion consequently concentrates on this process.

2.23 Polymerisation of Cyclosiloxanes

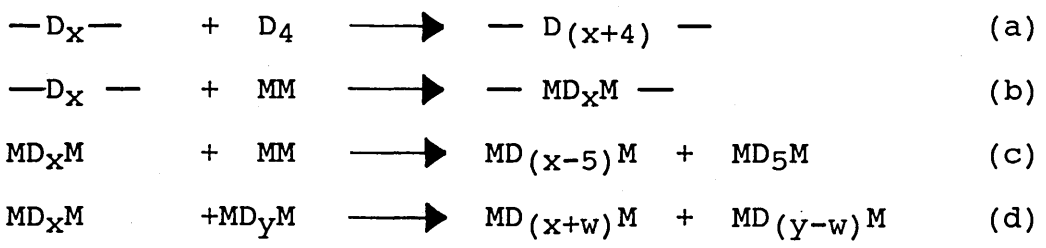
Organosiloxane cyclic and silanol oligomers are readily prepared by the hydrolysis of organochlorosilanes (56). The cyclics, predominantly x = 4 or 5, may be recovered by fractionation. However, the strained cyclic trimer is only present in low concentration and may be obtained in larger quantities by pyrolysis of higher polymer (57).



Reaction Scheme 2.3 Preparation of Cyclic Organosiloxane and Silanol Oligomers

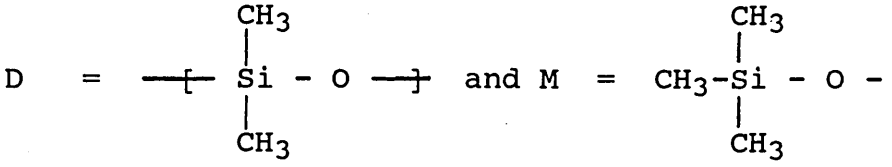
Linear polysiloxanes can be synthesised by both anionic and cationic ring opening polymerisation of cyclic siloxanes (58.59). The RMM of polymers is regulated by the incorporation of controlled amounts of monofunctional end blocking reagents into the system (41, 60 - 62). As a result of similar reactivities of siloxane bonds in the linear and cyclic species, the anionic or cationic catalysts attack both rings and chains during polymerisation. These so called "redistribution" or "equilibration" polymerisations involve reactions such as those listed in Reaction Scheme 2.4 occurring throughout

the process.



Reaction Scheme 2.4 Redistribution Reactions Occurring During a Siloxane Equilibration

It is convenient to use the well established shorthand scheme for dimethylsiloxane chemical structures. Here "M" denotes a monofunctional siloxane terminal unit whereas "D" refers to a difunctional siloxane unit i.e.

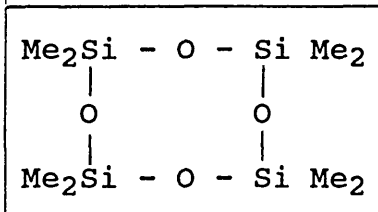
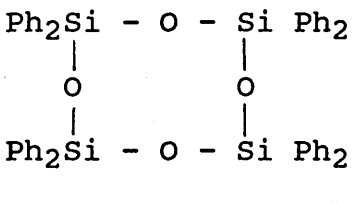


"D_4" therefore represents the cyclic siloxane tetramer while "MM" is the linear dimer. Some of the important terminology and nomenclature for siloxanes is given in Tables 2.4 and 2.5.

TABLE 2.4 Common Terminolgy of Siloxanes

Formula	Abbreviated Formula	Symbol
$(CH_3)_3Si\ O_{0.5}$	$Me_3Si\ O_{0.5}$	M
$(CH_3)_2Si\ O$	$Me_2Si\ O$	D
$CH_3Si\ O_{1.5}$	$Me\ Si\ O_{1.5}$	T
$CH_3(C_6H_5)Si\ O$	$MePh\ Si\ O$	D′
$(C_6H_5)_2\ Si\ O$	$Ph_2Si\ O$	D′
$(CH_3)\ HSi\ O$	$Me\ HSi\ O$	D′
$Si\ O_2$	$Si\ O_2$	Q

TABLE 2.5 Examples of Nomenclature

Structural [a] Formula	"MDT" Formula	Systematic [b] Name
$Me_3Si\ OSi\ Me_3$	MM	Hexamethyldisiloxane
$Me_3Si\ OSi\ Me_2OSi\ Me_3$	MDM	Octamethyltrisiloxane
$Me_3Si\ O(SiMe_2O)_2SiMe_3$	MD_2M	Decamethyltetrasiloxane
	D_4	Octamethylcyclotetra siloxane
	D'_4	Octaphenylcyclotetra siloxane
$(Me_3Si\ O)_3\ Si\ Me$	M_3T	1,1,1,3,5,5,5 - hepta methyl - 3 - trimethyl siloxy - trisiloxane
$Me_3Si\ O\ SiH\ Me\ OSi\ Me_3$	MD'M	1,1,1,3,5,5,5 - Heptamethyl trisiloxane

[a] Abbreviated [b] IUPAC

Since a variety of interchange reactions can take place, a quantitative conversion of cyclic species to high polymer is not achieved and there is, at thermodynamic equilibrium, a mixture of linear and cyclic species. In fact, these reactions result in a Gaussian distribution of molar mass among the chain molecules together with an approximately monotonically decreasing distribution of ring species as ring size increases (63 - 69) (Figure 2.2).

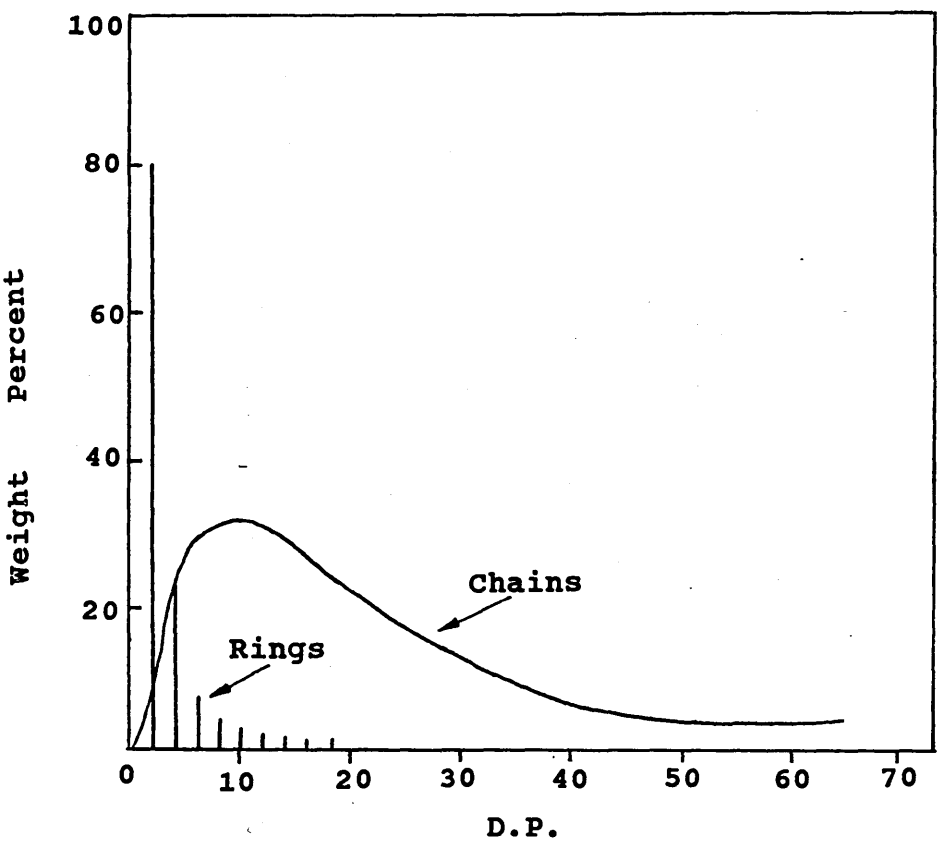
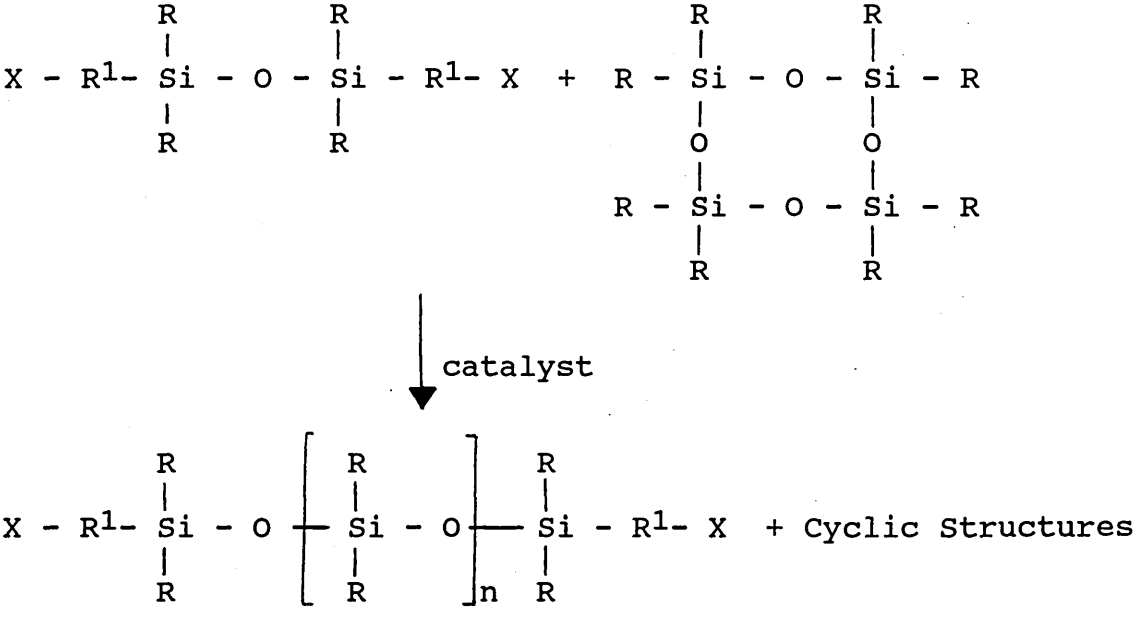


Figure 2.2 **Typical Molecular Distribution For A Ring-Chain Equilibrium Polymer (63)**

Rates of the processes depend upon factors such as catalyst type and concentration, temperature, pressure and the use of various types and amounts of promoters. With the exception of using organolithium catalysts in the anionic polymerisation of the D_3 monomer (70 - 72), significant amounts of redistribution cannot be avoided.

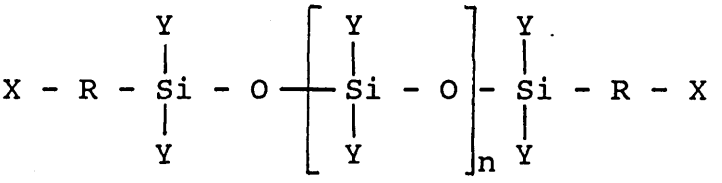
The experimental techniques involved in redistribution polymerisation are normally quite facile. The general method lends itself well to the laboratory synthesis of di-organo-functional siloxanes through variation of the structures of "R", "R^1" and "X" shown in Reaction Scheme 2.5.



Reaction Scheme 2.5 Synthesis of Functionally Terminated Siloxane Oligomers

It should be noted that during the equilibration process the catalyst can only cleave the Si - O bonds in the cyclic or linear species present including the "end blocker" and growing chains. The Si - R^1 or R^1- X bonds are unaffected. Therefore, at the end of the reaction the linear oligomers are functionally terminated and the minority cyclic side products (10 - 15 % in total) are non functional. After elimination of catalyst, the cyclic side products can usually be removed from the system by vacumm distillation at elevated temperatures.

The final linear product is an α, ω - difunctional siloxane oligomer and the general structure is shown in Scheme 2.6.

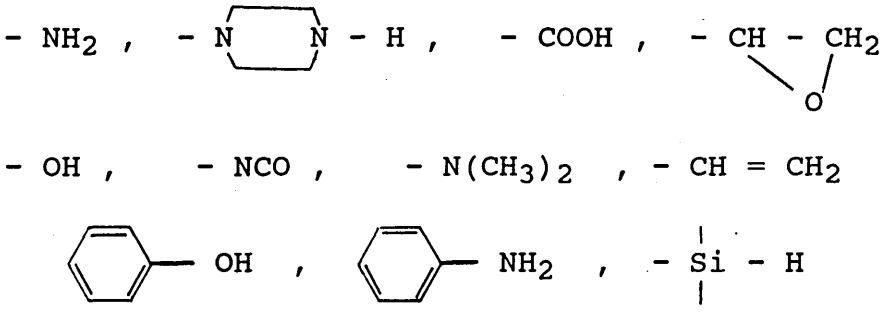


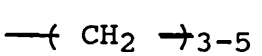
Scheme 2.6. General Structure of α, ω - Difunctional Siloxane Oligomer

In this structure X, R, Y and n can be varied and accordingly the resulting oligomers can have a wide range of properties such as chemical reactivity, molar mass, thermal and physical behaviour etc. A brief summary of possible variations is shown in Table 2.6 which shows the functional end groups, relative molar masses and backbone structures that have been prepared (41, 61, 62, 73 - 75).

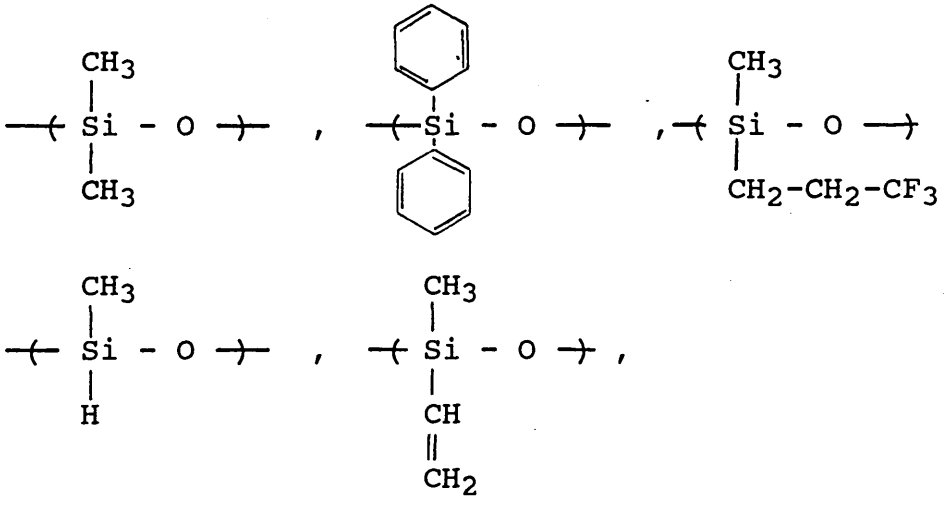
TABLE 2.6 Possible Variations in the Structure and Composition of Siloxane Oligomers.

X: Functional End Groups



R: 

Y: Backbone Composition



or their combinations.

n: Degree of Polymerisation 0 - 150 or higher

As expected, the nature of terminal functional groups determines the reactivity of siloxane oligomers towards other reactants. Variations in backbone compositions have critical effects on the glass transition temperature, solubility parameter, thermal stability and surface behaviour of the resulting oligomers (37,41,76,77). The average degree of polymerisation (n) mainly affects the morphology and phase separation behaviour of the copolymers derived from respective siloxane oligomers. This in turn determines the thermal, mechanical and solution properties, surface activity and processibility of the resulting multiphase materials.

There are many catalysts that can be used in the preparation of polysiloxane oligomers by equilibriation reactions. The choice of catalyst depends upon the temperature of the equilibration as well as the type of functional disiloxane that is used. For example, in preparing an aminopropyl terminated siloxane oligomer, a basic catalyst is used rather than an acidic catalyst as this would react with the amine end groups.

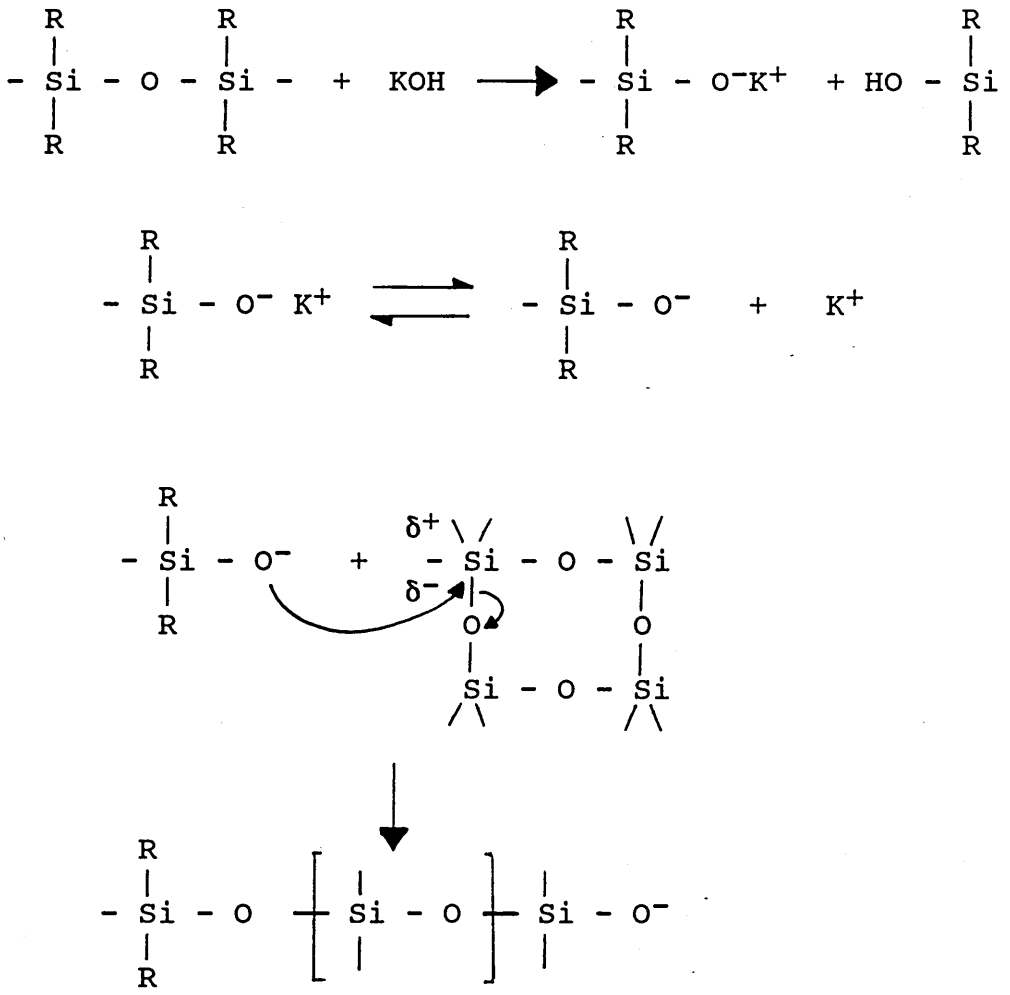
2.24 Anionic Polymerisation

Anionic ring opening polymerisations are usually carried out either in bulk or in solution. A wide range of catalyst types are active (for examples see reference, (37, 41,78,79)). Representative catalysts include hydroxides, alcoholates, phenolates, silanolates, siloxanolates of the alkali metals, quaternary ammonium and phosphonium bases.

Kantor and coworkers (60), suggested that nuleophilic attack on the silicon atom by a silanolate anion is the essential step in base catalysed dimethylsiloxane rearrangements. In accordance with this, Hurd et al (80) observed that KNH_2 and KOH were equally reactive in dimethylsiloxane polymerisations, indicating that -OH or $-NH_2$ constituted inactive terminal groups.

It is now believed that all basic catalysts generate the silanolate anion in situ and it is this species which breaks the silicon - oxygen bond in linear or cyclic siloxanes. The mechanism illustrated in Reaction Scheme 2.7 was proposed by Grubb and Osthoff (81) for anionic ring opening polymerisation.

Catalysts based on quaternary ammonium and phosphonium bases are referred to as transient catalysts, since they decompose above certain temperatures to products which are not catalytically active towards siloxanes (82, 83). An example of this type of catalyst is tetramethylammonium siloxanolate, prepared by the reaction of tetramethylammonium hydroxide with D_4 (82). This catalyst polymerises D_4 at temperatures up to ca 120°C. Above this temperature the catalyst decomposes fairly rapidly to trimethylamine and methoxy terminated siloxane.



Reaction Scheme 2.7 Mechanism for Anionic Ring Opening Polymerisation of Siloxanes

However, catalysts such as potassium siloxanolates are not transient. Non-transient catalysts must be neutralised or removed by some other method to give a thermally stable polymer. If the catalyst is not removed it may cause depolymerisation at high temperatures. Non-transient catalysts can often be used at much higher temperatures than transient catalysts, leading to faster rates of reaction.

Rates of anionic polymerisation are influenced by the

number of siloxane units present in the monomer rings. Cyclotrisiloxanes polymerise faster than the cyclotetrasiloxanes owing to ring strain in the three unit rings. For dimethylsiloxanes, D_3 reportedly polymerises approximately fifty times faster than D_4 (71). Kantor et al (60) found the following order of reactivity for basic catalysis of dimethylsiloxane rearrangement.

Many compounds with electron donor characteristic are reported to have an accelerating effect on anionic polymerisation. Representative "promoters" reported include tetrahydrofuran (84 - 86), dimethylformamide (87) and sulfoxides (88,89).

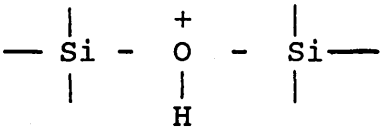
2.25 Cationic Polymerisation

Cationic polymerisation of cyclosiloxanes is used much less frequently than anionic reactions. Acidic catalysts most frequently used include sulphuric acid and its derivatives (90, 91). Weaker organic acids are generally ineffective. Trifluoroacetic acid is an acid of moderate strength however, and this has been used in mechanistic investigations of cationic siloxane ring opening reactions as well as to polymerise D_4 in bulk (92, 93).

Kantor et al (60) observed the following order of reactivity for the acid catalysed polymerisation of dimethylsiloxanes.

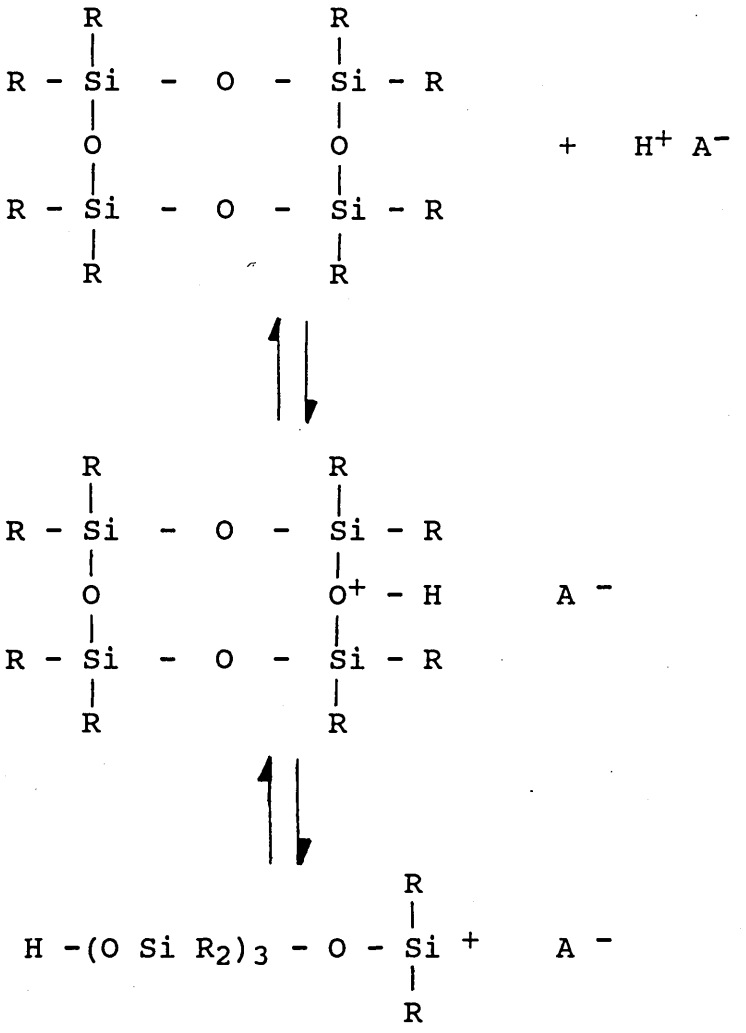
$$\square D_3 \square > MM > MDM > MD_2M > \square D_4 \square$$

This sequence was later substantiated by other workers (94, 95). From this they concluded that susceptibility of the siloxane link to cleavage by acids correlated with the basicity of the siloxane oxygen atom. Siloxane oxygens lying close to terminal alkyl groups should be the stronger electron donors. Thus Kantor and coworkers concluded that attack of protonic acids on siloxanes involved the intermediate structure.

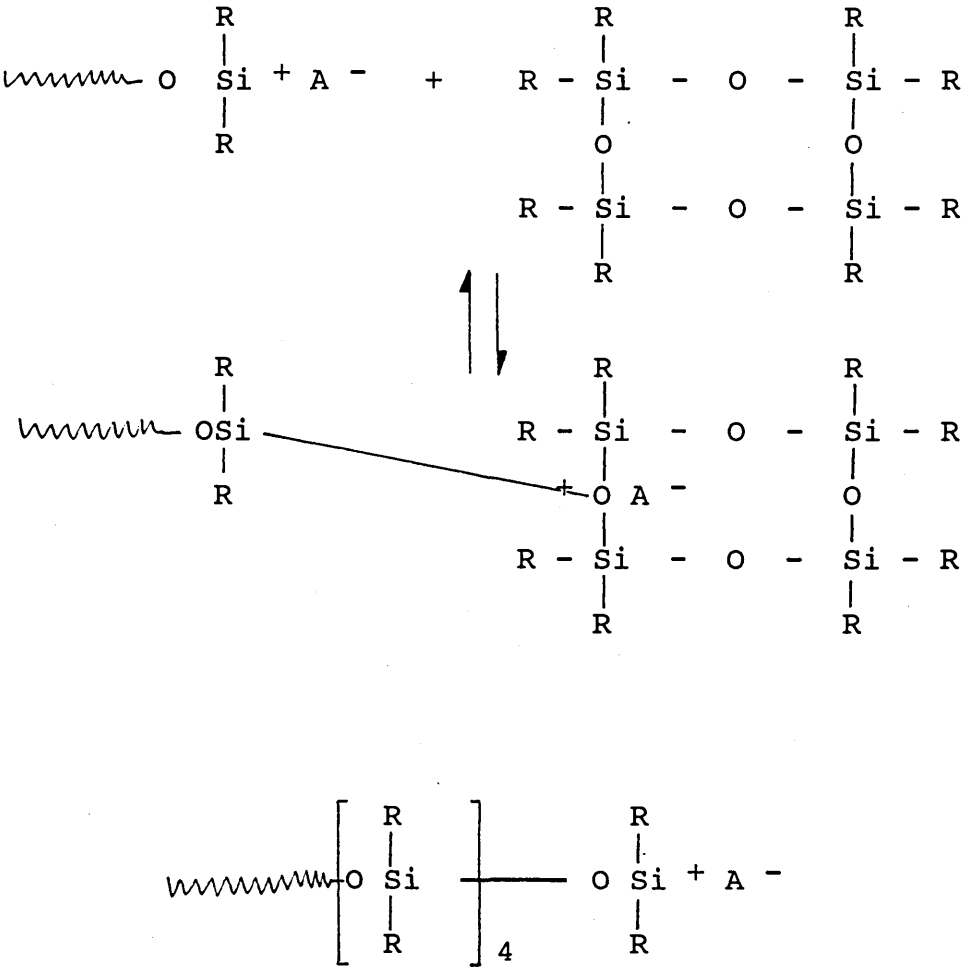


The mechanism for acid catalysed polymerisation is thought to be that shown in Reaction Scheme 2.8. However, Odian (96), believes there is no evidence for the rearrangement of the siliconium ion shown in this reaction scheme. Alternatively it could be proposed that the propagating species is the tertiary oxonium ion.

Initiation



Propagation



Reaction Scheme 2.8 Mechanism for Acid Catalysed Ring Opening Polymerisation

2.3 Polysiloxane Containing Block Copolymers

Siloxane containing multiphase copolymers have been described extensively in the literature over the past twenty five years (11, 40, 51, 76, 97 - 99). The main interest in these type of block or segmented copolymers arises because multiphase organsiloxane copolymers have many desirable properties including low temperature flexibility, thermal and uv stability, low surface energy and high gas permeability, which are quite different from those of conventional rubbery hydrocarbon polymers.

Development of methods for the synthesis of copolymers containing well defined polysiloxane blocks dates from the early 1950's (97). Further interest was created by the discovery of the ability of poly(dimethylsiloxane) - poly(oxyalkylene) copolymers to stabilise flexible polyurethane foam formation.

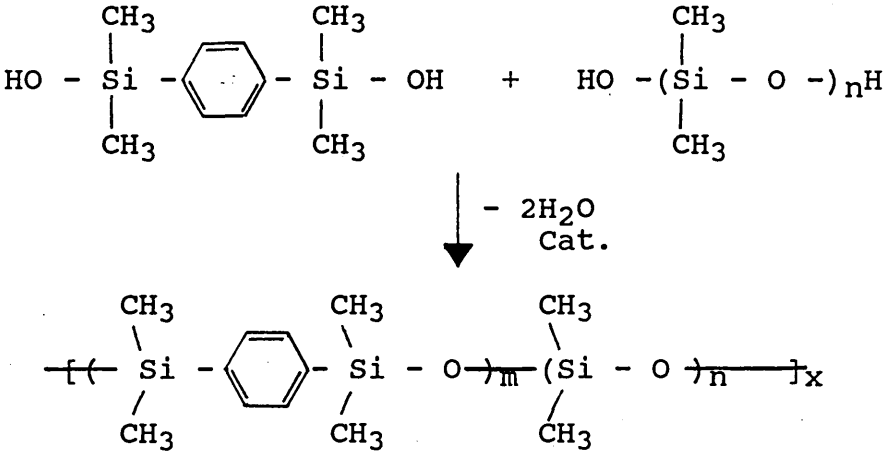
There are a variety of methods by which siloxane containing block or segmented copolymers can be synthesised. However, before considering these, two factors should be noted. The first arises from the susceptibility of the Si - O - Si linkages to undergo scission and bond reformation by the action of strong bases and acids. These processes as previously mentioned can lead to a randomisation (equilibration) of siloxane units between polysiloxane chains and hence to a broadened distribution of relative molar masses (RMM's), and often to the liberation of polysiloxane homopolymer, either during synthesis or on

subsequent contact with acids or bases. Therefore care has to be taken in the selection of initiators or catalysts used in the synthesis of siloxane copolymers.

The second factor relates to the mode of attachment of polysiloxane units to the other components in the block copolymers. Si - O - C connections are relatively readily hydrolysed and in the interests of product stability, are better replaced where possible by the more stable Si - C bonds (76, 100, 101).

2.31 Randomly Coupled Siloxane Copolymers

The principle of random block polymerisation has been utilised for polysiloxane block copolymer synthesis in many varied systems. Multiblock polymers which have p - phenylene groups in the main chain were synthesised by condensation between two types of silanol groups as shown in Reaction Scheme 2.9 , (102, 103).



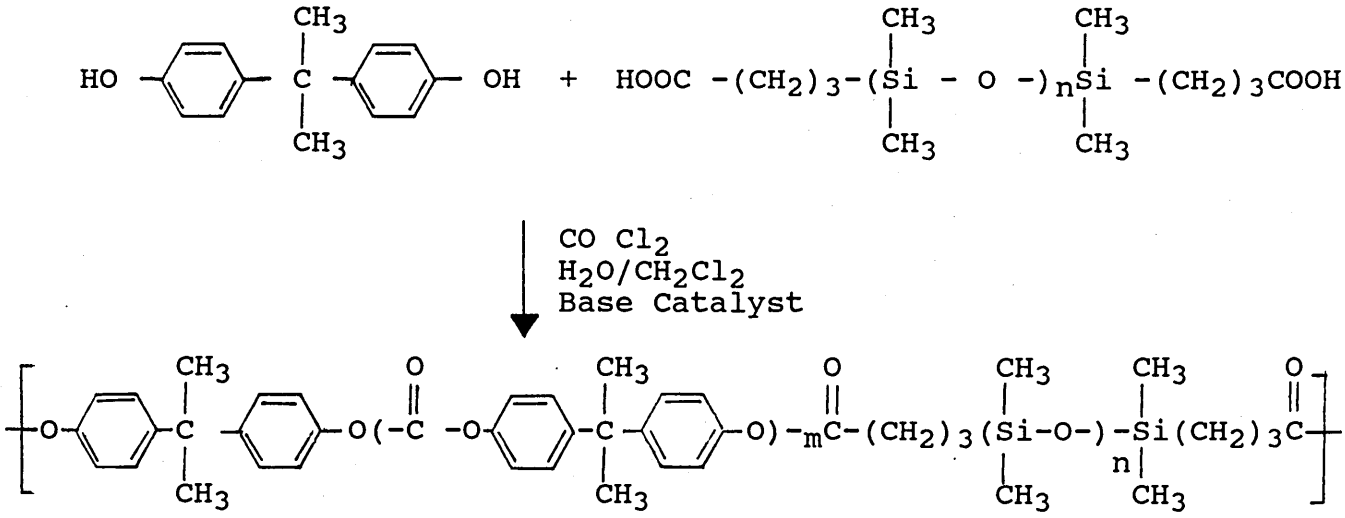
Reaction Scheme 2.9 Synthesis of Siloxane - Silarylene-Siloxane Copolymers (103)

The reaction was catalysed by weak bases such as hexylamine carboxylate salts or tetramethylguanidine to avoid Si - O

bond randomisation.

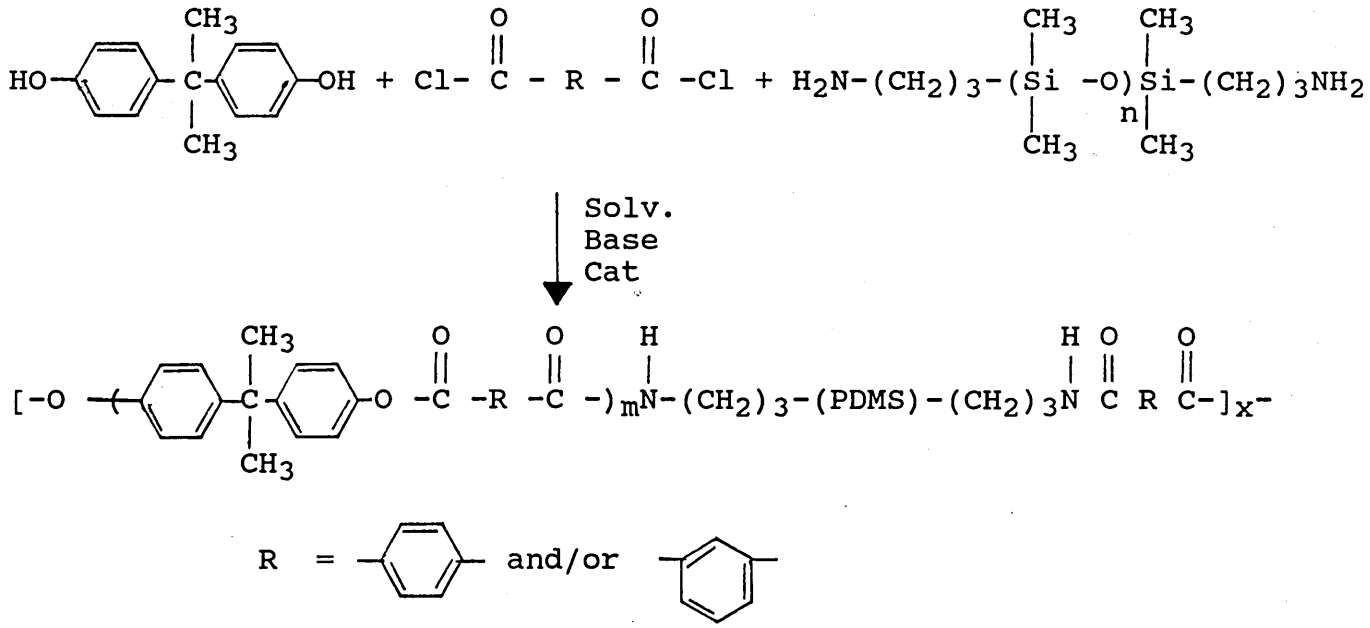
Another approach is for the polysiloxane to be furnished with functional organic end groups which are employed in subsequent conventional polycondensation reactions. Randomly coupled polycarbonate - PDMS block copolymers were first synthesised by Vaughn et al(104, 105), by the phosgenation of a mixture of bisphenol-A and a dichlorosilane terminated polydimethylsiloxane oligomer in the presence of pyridine. The copolymers produced by this process are alternating, but randomly coupled, block copolymers with fairly disperse polyester segments since the method used provides little control over the in situ formation of the polycarbonate blocks.

Randomly coupled polycarbonate/polysiloxane block copolymers containing the hydrolytically more stable Si - C link have been synthesised using an interfacial phase transfer catalysed technique (75, 106, 107). The general synthetic route used preformed carboxypropyl terminated polydimethylsiloxane oligomers with bisphenol-A and phosgene. This was carried out in the presence of a strong base and a phase transfer catalyst, in a water/dichloromethane solvent system (75, 106), as shown in Reaction Scheme 2.10.



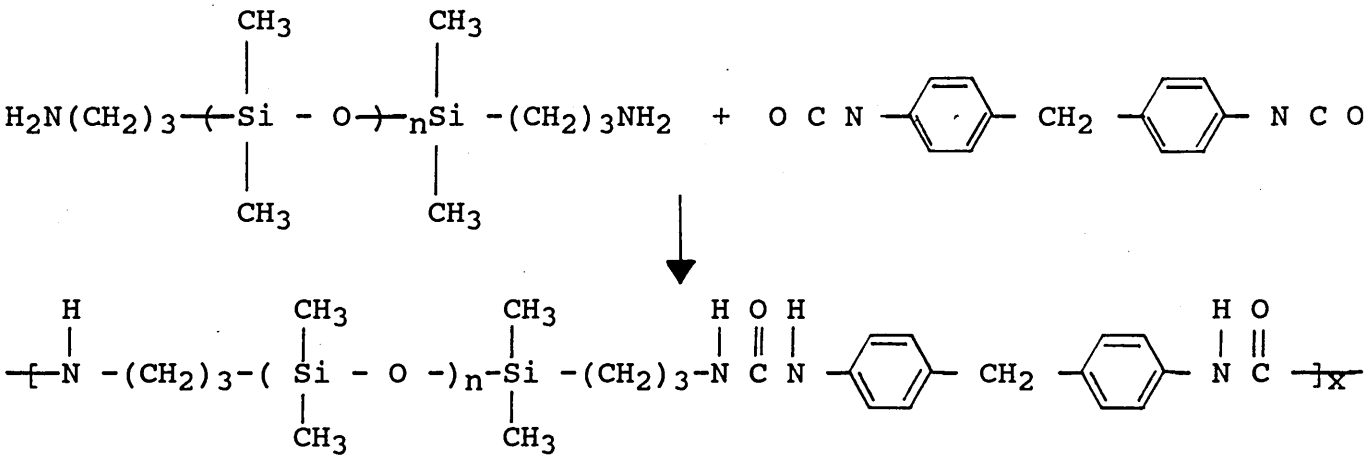
Reaction Scheme 2.10 Synthesis of Bisphenol - A Carbonate Siloxane Segmented Copolymers (106)

Using a similar interfacial procedure random copolymers of polyarylester - polydimethyl siloxane were synthesised by reacting an aminopropyl terminated polysiloxane with bisphenol A, terephthaloyl chloride and isophthaloyl chloride (108 - 110). The polyarylester block, like the polycarbonate block, is synthesised in situ during the copolymerisation reaction, so the control of the block size is not very precise. As aminopropyl terminated siloxane oligomers are utilised, the linkages which connect the respective blocks are amide linkages, as illustrated in Reaction Scheme 2.11



Reaction Scheme 2.11 Synthesis of Poly(Aryl Ester) Polysiloxane Segmented Copolymers(109)

Siloxane - urea segmented copolymers have been prepared also. The first example of this class of material was synthesised by the direct reaction of aminopropyl terminated polydimethylsiloxane oligomers and 4, 4 - diphenylmethane diisocyanate (MDI) in solution at room temperature as shown in Reaction Scheme 2.12.

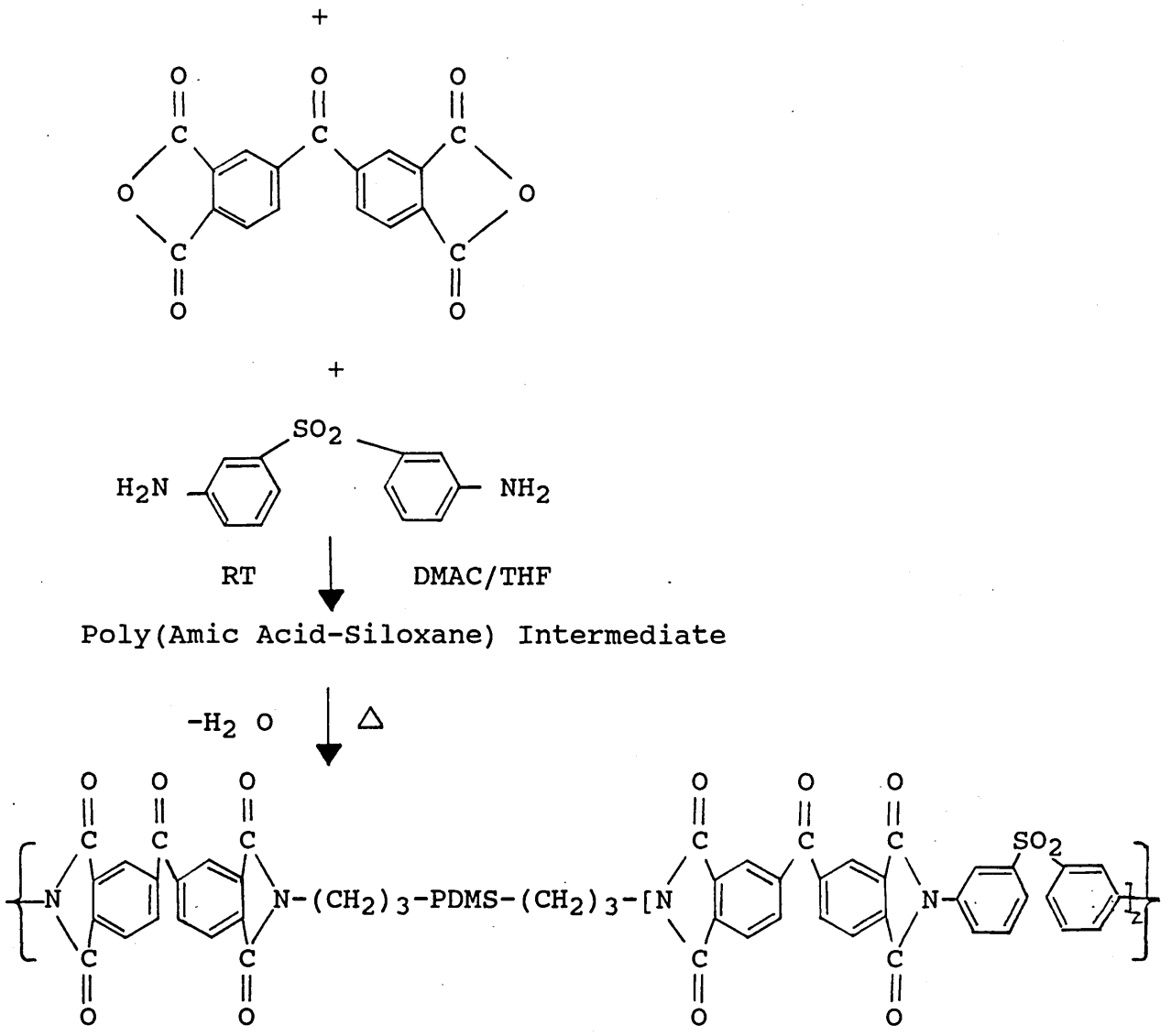


Reaction Scheme 2.12 Synthesis of MDI Based Siloxane-Urea Segmented Copolymers (111)

Bis - p(isocyanato cyclohexyl)- methane and tolylene diisocyanate (TDI) based siloxane - urea copolymers have also been described in the literature (112, 113).The reaction between α, ω diisocyanate - terminated polyurea oligomers, (which were performed from α, α′ - dianilino-p-xylene and MDI in anisole) with α, ω - aminopropyl PDMS results in formation of multiblock copolymers. These are claimed to have enhanced solubility over exisiting PDMS - poly(urea) copolymers, in organic solvents (114).

Recently, randomly coupled poly(siloxane - imide) copolymers have become prominent due to various unique properties displayed by these materials. These properties include fracture toughness, enhanced adhesion, improved dielectric properties, increased solubility and excellent atomic oxygen resistance (115). The copolymers were synthesised from aminopropyl terminated PDMS benzophenonetetra- carboxylic acid dianhydride (BTDA) and pyromellitic dianhydride (PMDA). In some reactions aromatic meta linked diamines such as oxydianiline have been used at varying levels as "chain extenders", to increase the aromatic content (and the thermal stability) of the resulting systems. For the synthetic procedure a cosolvent system was employed to achieve complete solvation of all components throughout the polymerisation and to ensure high molar mass products were obtained. A thermal procedure was used to convert the poly (amic acid siloxane) intermediates to the corresponding poly (imide siloxane)

block copolymers. The reactions are illustrated in Reaction Scheme 2.13.

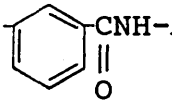
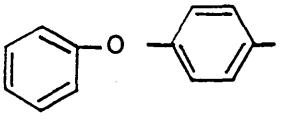


Reaction Scheme 2.13 Synthesis of Siloxane - Imide Segmented Copolymers (116, 117)

2.32 Siloxane Copolymer Synthesis by Oligomer Combination

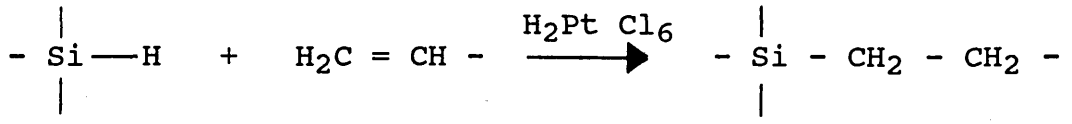
The next class of reactions to be considered is that yielding polysiloxane block or segmented copolymers by oligomer combination some examples of this mode of copolymer formation are illustrated in Table 2.7.

TABLE 2.7 (118) Polysiloxane Block Polymers by Oligomer Combination Reaction

Polysiloxane Oligomer	Additional Oligomers & other Reactants	Product Type
Cl[PDMS] $Si(CH_3)_2Cl$	$HOSi(CH_3)_2PSt\ Si(CH_3)_2OH$ /Pyridine	PDMS-b-(119) Polyst yrene
Cl[PDMS]$Si(CH_3)_2Cl$	$HO(CH_2)_6O[CO(CH_2)_8CO(CH_2)_6O]_nH$ /Pyridine	PDMS-b-Polyester (120,121)
Cl[PDMS]$Si(CH_3)_2Cl$	Hydroxyl-ended poly(ethylene adipate-co-maleate)N-methyl morpholine	PDMS-b-unsaturated polyester (122)
HO[PDMS]$Si(CH_3)_2OH$	$HO[CH_2CH_2]_nOH$/tin(II) Octoate	PDMS-b-Polyethylene (123)
$HOOC(CH_2)_{10}$[PDMS]-$Si(CH_3)_2(CH_2)_{10}COH$	H_2N-Ar-NH(C(=O)-  -C(=O)-NH-Ar-NH)$_x$H Ar: 	PDMS- b-Aromatic Polyamides (124)

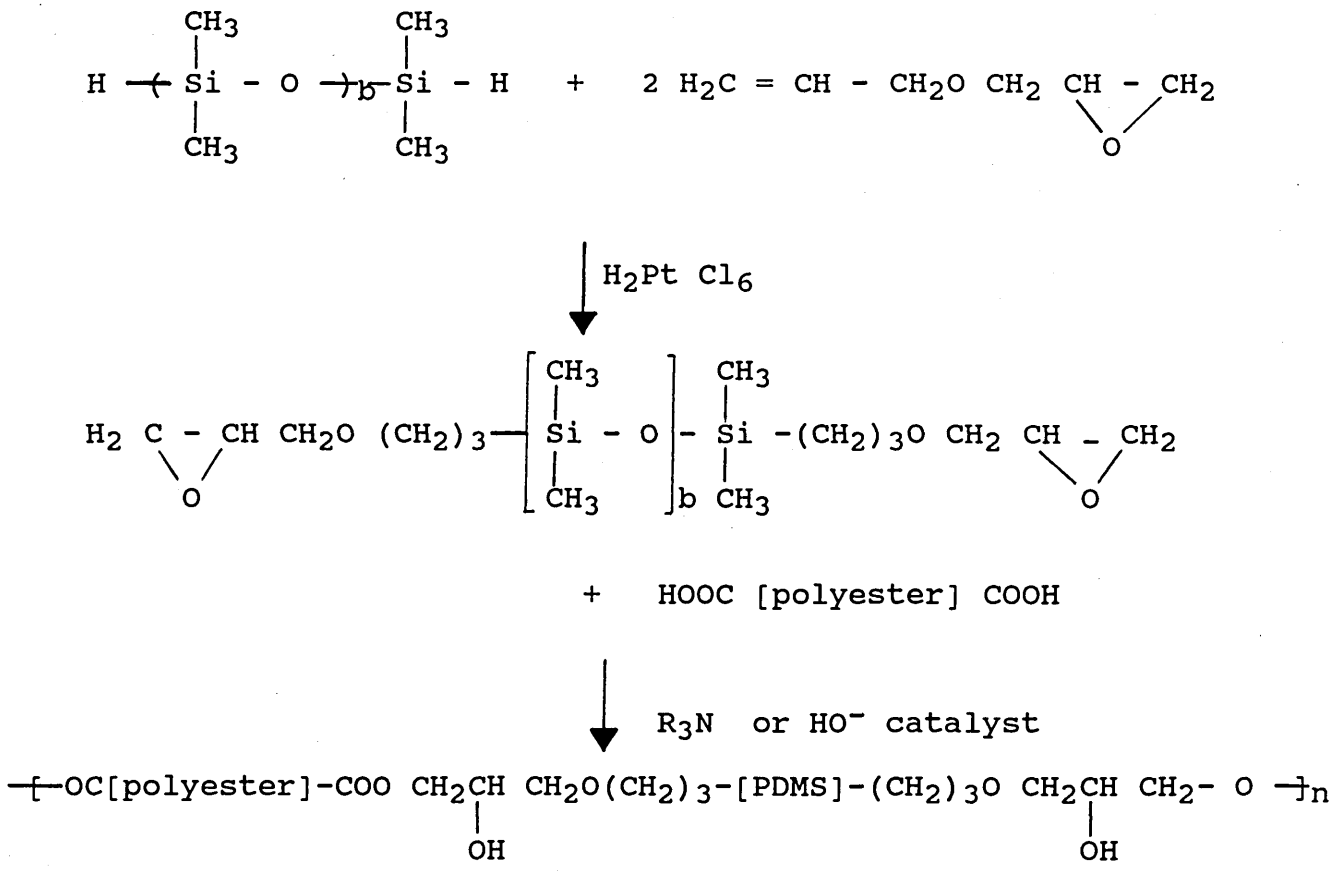
These oligomer combination reactions are supplemented by two types of reaction that are specific to organosilicon chemistry.

The first is the addition reaction which occurs between hydrosilane and vinyl groups, usually catalysed by chloroplatinic acid (125 - 127), forming Si - C bonds. This is known as hydrosilation and is depicted in Reaction Scheme 2.14.



Reaction Scheme 2.14 Hydrosilation (125)

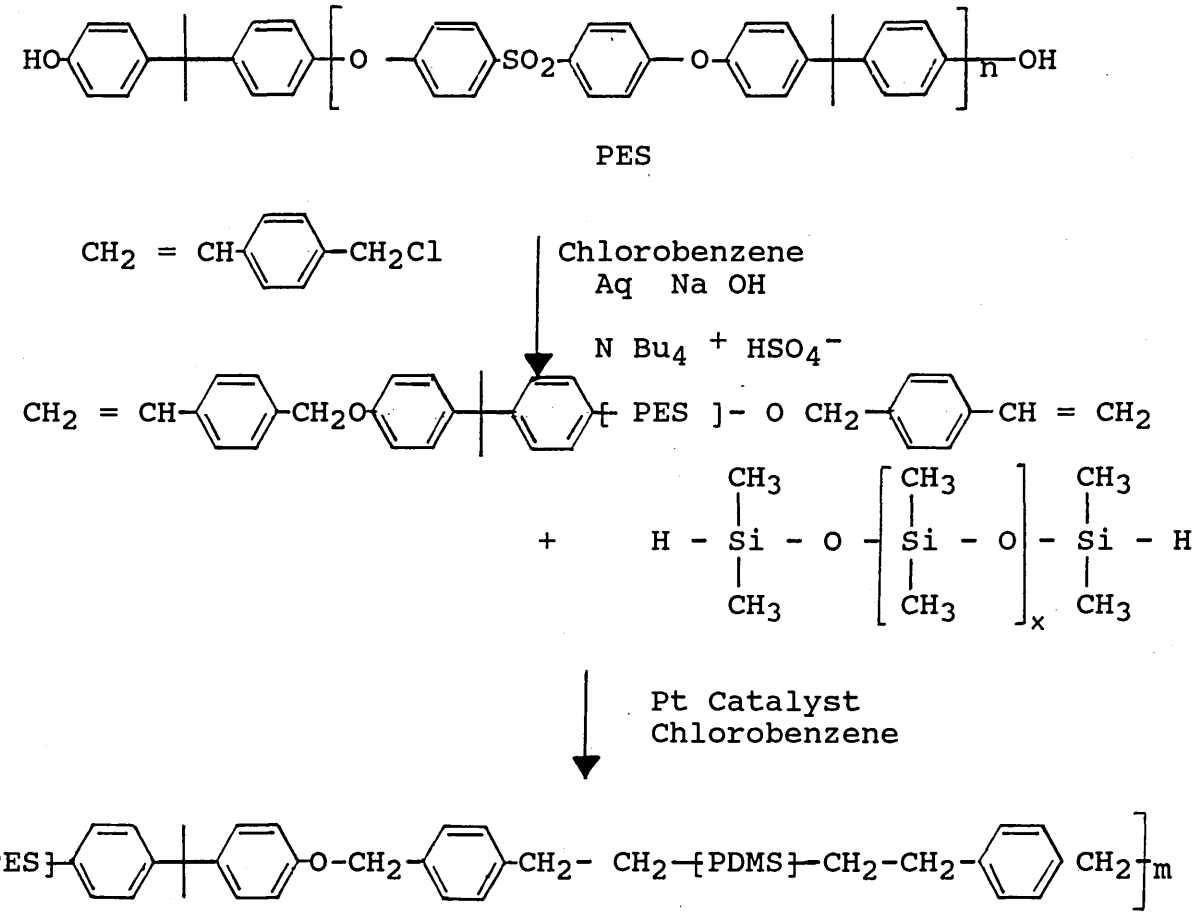
This reaction can be adapted to block copolymer formation in various ways, e.g. by forming polystyrenes with $Si(CH_3)_2CH = CH_2$ or $- CH_2Si(CH_3)_2CH = CH_2$ end groups and combining these with mono - or dihydro - ended siloxane oligomers, or conversely by reacting α, ω (hydro dimethyl(silyl)) polystyrenes with siloxane oligomers having allyloxy end groups (128 - 130). Another technique uses the hydrosilation reaction to attach epoxide end groups to a siloxane chain. This produces oligomers which can form block copolymers by ring opening polyaddition to carboxyl-ended unsaturated polyesters (100), as shown in Reaction Scheme 2.15.



Reaction Scheme 2.15 Polysiloxane - Unsaturated Polyester Copolymers

A further block copolymer formation performed in a similar way, is the synthesis of poly(sulphone - b - siloxane). The use of Pt -catalysed hydrosilation was first applied to this copolymer synthesis by Gagnebien (131 - 133), and involved either coupling of α, ω di(hydroxy phenyl) polysulphone with α, ω di(epoxy) PDMS, (produced from hydrosilation of 1 - allyloxy - 2, 3 - epoxypropane with α, ω di(hydrosilane) PDMS, (131)), or coupling of α, ω - di(1 - allyloxy - 2 - hydroxy-propyl) polysulphone with α, ω di(hydrosilane) PDMS (132). Both routes yielded hydrolytically stable Si - C linkages between the two blocks, but unfortunately copolymers of only low molar mass.

Alternating block copolymers of aromatic poly(ether sulphone) and PDMS of high molar mass have been prepared via hydrosilation. This involved the reaction between α,ω di(vinyl benzyl) polyether sulphone or α, ω di(allylether) polyether sulphone with α, ω di(hydrosilane) PDMS (134) and is illustrated in Reaction Scheme 2.16

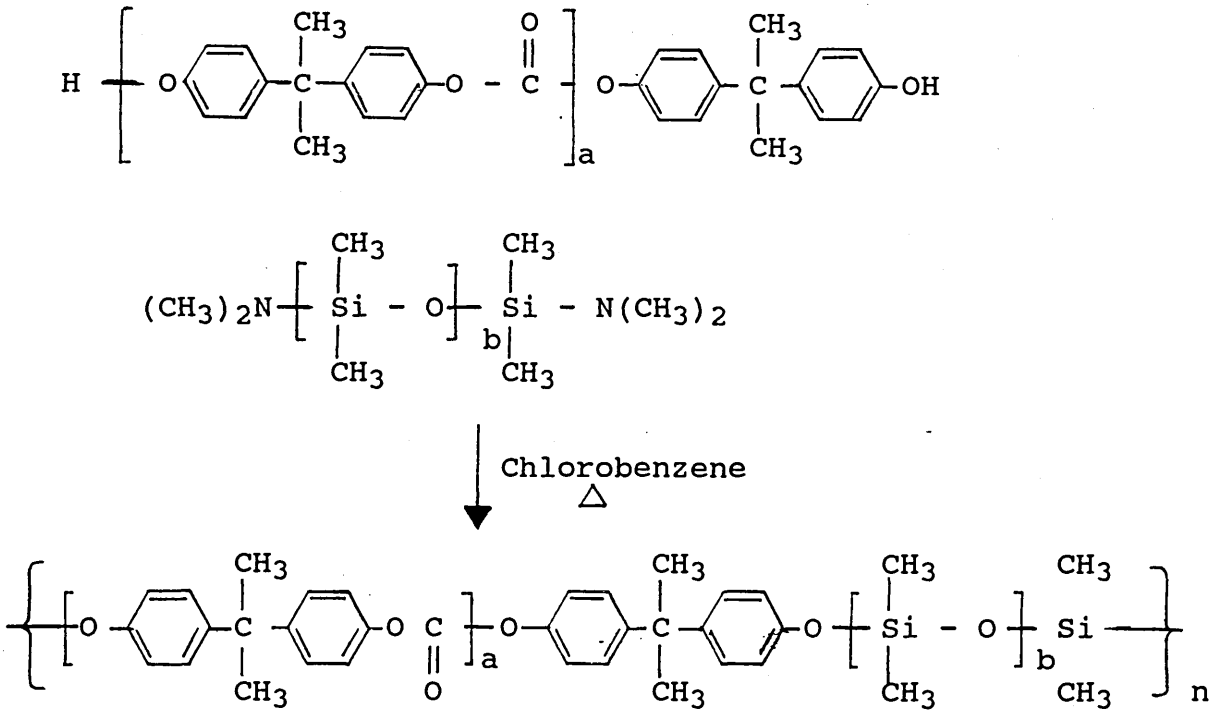


Reaction Scheme 2.16 Synthesis of Polyether Sulphone PDMS Alternating Block Copolymers (134)

The vinyl functionalised polyether sulphone was prepared via the phase transfer catalyzed etherification of α, ω di(hydroxyphenyl) polyether sulphone with p- chloromethyl styrene or allybromide (135).

The second reaction specific to organosilicon chemistry is the condensation reaction between dialkylamine terminated siloxane oligomers and hydroxyl ended co-reactant oligomers; dialkylamine is eliminated as Si - O - C bonds are formed. The hydroxyl groups of the coreactants may be phenolic or alcoholic, the former being the more reactive. This approach has been used to obtain multiblock polymers of PDMS with a variety of other species.

Noshay and co-workers (83, 136) initially developed the hydroxyl-silylamine condensation reaction as a route to perfectly alternating PDMS polysulphone copolymers. This functional end group chemistry has been applied to a variety of siloxane copolymer systems. These include polyarylester (109, 137) tetramethyl - p - silyphenylene siloxane (138), aliphatic polyester (120, 121), poly(xylenyl ether)(139),poly(ether etherketone)(140) and the extensively studied polycarbonate system (83, 141) of which the synthetic route is illustrated in Reaction Scheme 2.17.



Reaction Scheme 2.17 Synthesis of Polycarbonate - Polydimethylsiloxane Block Copolymers (141)

The main advantage of the silylamine - hydroxyl route is the preparation of perfectly alternating block copolymers from preformed well defined oligomers of the individual blocks. A disadvantage of this route, as with any combination of mutually reactive oligomers is the need to synthesise each of the blocks and then copolymerising them into the final block copolymer. A second disadvantage is that this route produces a copolymer containing an Si- O - C link rather than the more hydrolytically stable Si - C bond, (100, 122).

2.33 Siloxane Copolymer Synthesis by Anionic Polymerisation

Ring opening polymerisation has been employed as the basis of another general approach to the synthesis of siloxane block copolymers in this case by the anionic polymerisation of cyclopolysiloxanes in ways which yield either polysiloxane - b - polysiloxane products or those containing polysiloxane and other structural classes of blocks.

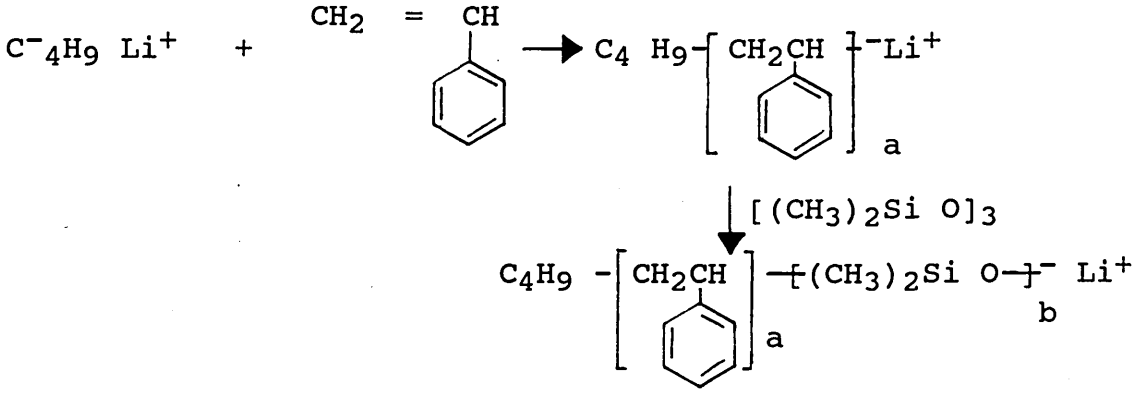
However, the tendency of siloxane bonds to undergo cleavage in strongly basic or acidic conditions imposes the need for a specific choice of polymerisable cyclopolysiloxane and of the initiator counterion if well defined products are to result. The most readily available monomer D_4, is partially susceptible to bond randomisation. However, this can be avoided by the use of the cyclic trimer, hexamethyl cyclotrisiloxane (D_3).

As shown earlier in this chapter, under certain conditions, D_3 polymerises to give linear polymers of negligible cyclosiloxane content and of narrow molar mass distribution at a much more rapid rate than D_4, (71). This can be explained by the ring strain of D_3, which enhances the reactivity of the Si - O bonds. Through this greater reactivity D_3 is open to polymerisation by weaker bases such as lithium silanolates or the lithium salts of hydrocarbon polymer anions, which do not promote the equilibration reaction. The presence of aprotic,

moderately electron donating compounds, such as tetrahydrofuran, glycol ethers and anisole are effective in promoting the polymerisation rate.

Controlled syntheses of diblock and triblock copolymers of diphenylsiloxane and dimethylsiloxane have been reported, (142), in which lithium based initiators were used in conjuction with the cyclic trimers of dimethyl and diphenyl siloxane. A similar procedure is applied in the synthesis of di and triblock copolymers of (fluoroalkyl,methyl) siloxane and dimethylsiloxane in which butyllithium is used as an initiator (76).

Styrene - dimethylsiloxane di and triblock copolymers have been synthesised by the anionic polymerisation of D_3 in toluene /THF solutions. Butyllithium is used as the initiator to form the polystyryl anion which is capable of initiating siloxane polymerisations (143 - 145).



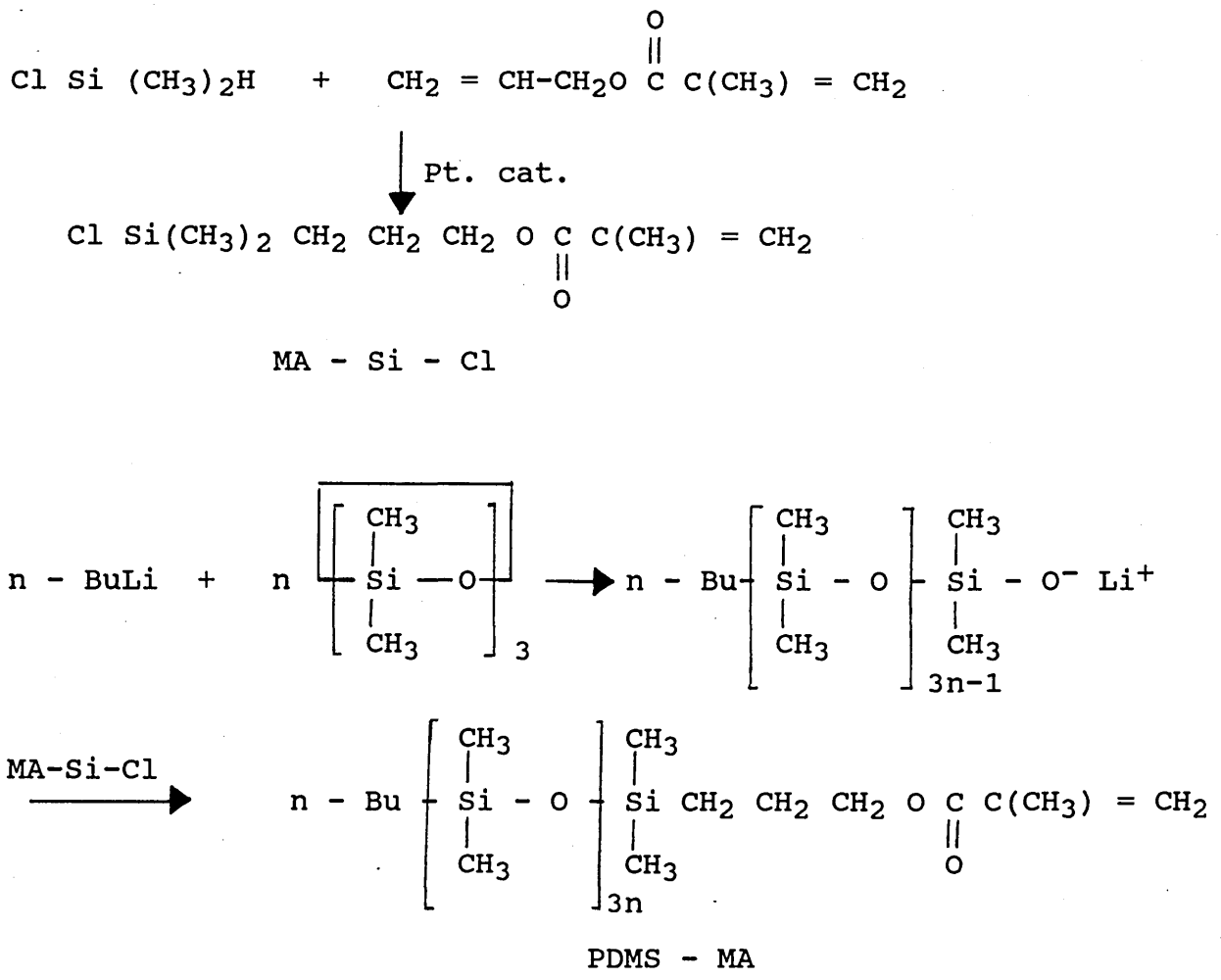
Reaction Scheme 2.18 Preparation of PDMS - Polystyrene AB Block Copolymers

This approach is further utilised in analogous polydiene materials giving rise to polydiene PDMS block copolymers

(146, 147).

Silanolate end groups are not themselves sufficiently nucleophilic to initiate the polymerisation of vinyl monomers and the approach cannot, therefore be extended to the direct synthesis of ABA copolymers with PDMS units as the central segments. To obtain such materials, recourse must be made to the coupling of silanol or silanolate ended diblock polymers by reagents such as $(CH_3)_2Si\ Cl_2$ or $(C_6H_5)_2-Si-(O-COO-CH_3)_2$, (148, 149). Yilgor et al synthesised novel A - B - A copolymers of PDMS/ polycaprolactone and PDMS /poly(2 - ethyloxazoline). The copolymers were prepared by the ring opening polymerisation of caprolactone and 2 - ethyloxazoline using hydroxyl alkyl and benzyl halide terminated siloxane oligomers respectively as the initiator and macromonomer (150).

Cameron (151), utilising the ability of D_3 to be polymerised anionically to give polymers of narrow MMD, synthesised methacrylate terminated siloxane macromers of various molar mass as represented in Reaction Scheme 2.19.



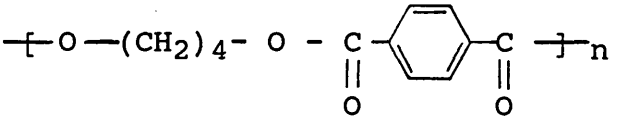
Reaction Scheme 2.19 Synthesis of Methacrylate Terminated Siloxane Macromers (151)

The copolymerisation of these methacrylate - ended PDMS macromers with styrene yields graft copolymers comprising a polystyrene backbone with PDMS side chains. Cameron extended the procedure to acrylonitrile to form siloxane acrylonitrile copolymers (152). Smith et al (153, 154) have applied the macromer technique to alkyl methacrylates to form well defined graft copolymers of polydimethylsiloxane side chains and polyalkyl methacrylate backbones.

2.4 Polybutylene Terephthalate

Poly(butylene terephthalate) (PBT) is a thermoplastic polyester, a condensation product that is characterised by many ester linkages distributed along the polymer backbone. PBT was first introduced commercially in 1968. It is characterised by excellent mould flow and short moulding cycles with excellent chemical resistance and performance at elevated temperatures. The appeal of PBT is in its very rapid and extensive crystallisation at mould temperatures below 100°C which ensures it is an excellent injection moulding material for engineering applications (4). It is also characterised by very good mechanical and electrical characteristics, excellent solvent resistance and good hydrolytic stability.

The polymer chain of PBT consists of a mixed aliphatic - aromatic structure:



2.41 Properties

PBT and polyesters in general are free of toxic combustion products other than carbon monoxide. The melting point of PBT is between 222 - 232°C depending on sample preparation and degree of annealing. The polymer contains no incorporated impurities, since the main by product of the polymerisation, i.e. tetrahydrofuran, is non-reactive and volatile under polymerisation conditions. PBT undergoes a unique reversible crystalline transformation at low levels

of applied stress (155 - 157). The transition is related to a conformational change of the butylene chain from a relaxed gauche - trans - gauche to a stretched all trans form. As a direct consequence of this transition, oriented PBT monofilaments show unusually high resilience and toughness which are important characteristics in such applications as tooth brush and paint brush bristles and filter fabrics (158). The glass transition temperature of PBT depends on degree of crystalline annealing, and method of measurement. Reported values are between 30° - 50°C (159), although crystallisation of quenched PBT samples occurs as low as 20°C (160).

PBT is one of the fastest crystallising polymers and is particularly suited for extrusion and injection moulding applications in which the high rate of crystallisation assures short processing cycles and excellent postforming dimensional stability.

The widespread acceptance of semi-crystalline thermoplastic polyesters generally is attributable to their physical, mechanical and electrical properties. PBT's fast mould cycle times gives parts that maintain mechanical integrity almost to the crystalline melting point. Also it displays excellent chemical resistance and hydrolytic stability. Enhancement of mechanical properties may be achieved with a variety of additives. The additive most widely used i.e. glass fibres, produces a two to six fold increase in flexural modulus and a concommitant increase in heat

deflection temperature. Additional factors that favour polyesters over other plastics include surface properties, toughness , low water absorption and thermal stability for continuous use at high temperatures.

The surfaces of moulded polyesters are glossy, hard and abrasion resistant, with low coefficients of friction. The surface shows little effect from abrasion with other materials or contact with solvents, even without lubricants or surface coatings. The toughness of the unfilled materials is shown by the no break results in the unnotched Izod test and high Gardner (falling dart) impact in unreinforced resins. However, they are notch-sensitive materials and, therefore, sharp corners or other built-in stress concentrators should be eliminated during production design. The low moisture absorption allows the material to maintain excellent dimensional stability through extremes in temperatures and humidities.

By virtue of its semicrystalline nature, PBT is highly resistant to a broad range of chemicals. It is degraded by aqueous alkalies and concentrated sulphuric and nitric acids. Chlorinated hydrocarbons have a tendency to swell the semi crystalline material, for which few simple solvents exist. The base electrical characteristics of PBT, coupled with its ability to tolerate modification has resulted in its extensive utilisation in the electrical and electronics markets which traditionally has been the domain of thermoset resins (161). PBT responds favourably to the

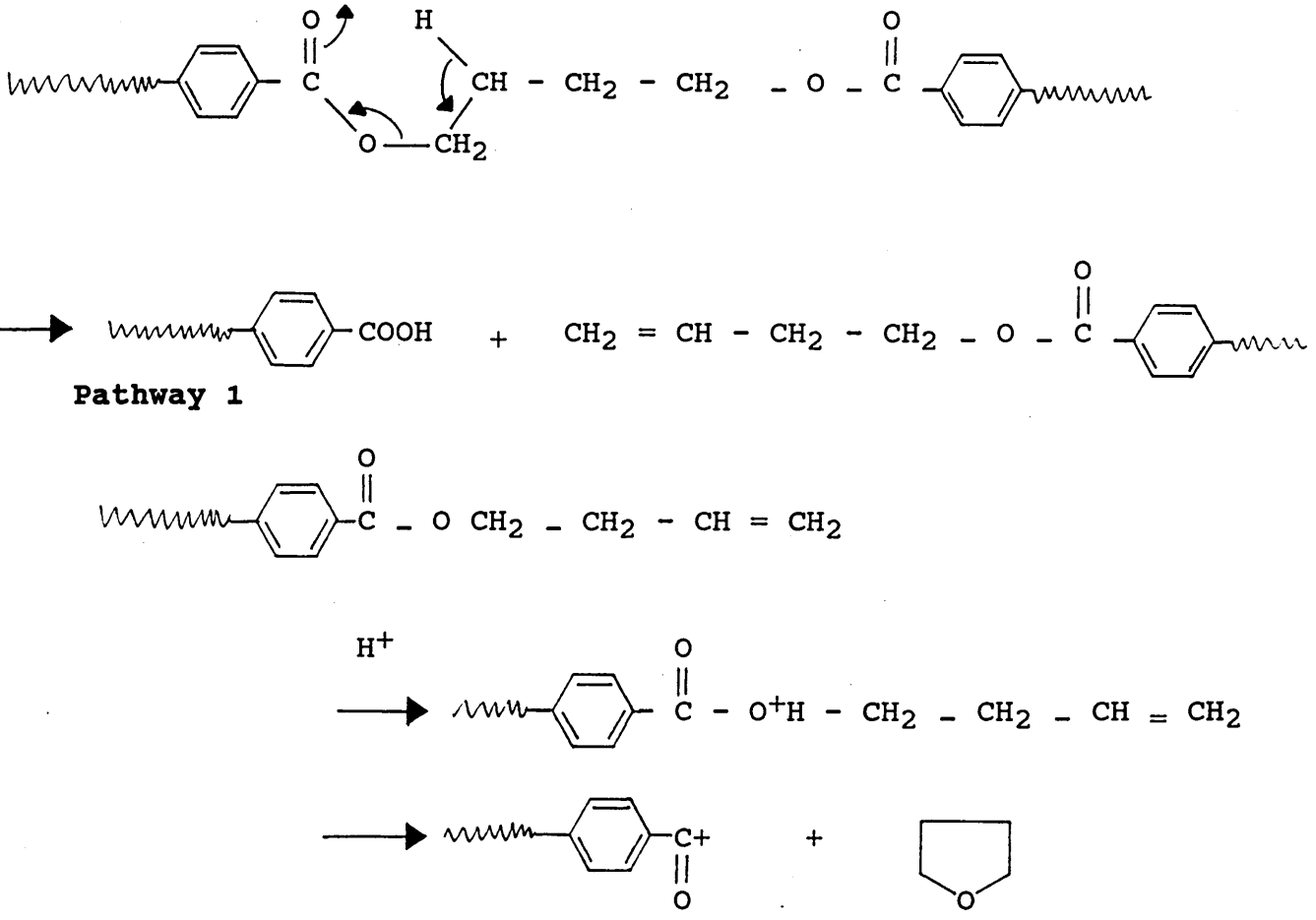
addition of uv stabilizer, with 90 - 100% retention of mechanical properties after five years of outdoor ageing.

2.42 Manufacture

PBT is made by the ester interchange reaction between 1, 4 - butanediol and dimethyl terephthalate, followed by polymerisation under high temperature and vacuum, with the removal of excess butanediol until high molar mass is achieved. Catalysis for both stages is provided by titanium orthoesters.

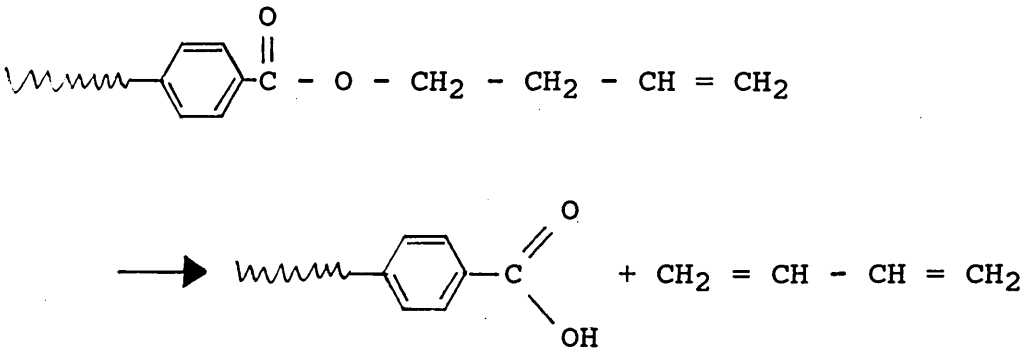
The principal by product of the production of PBT is tetrahydrofuran, which forms through intramolecular cyclisation of terminal 4 - hydroxybutyl esters. Fortunately with the high temperature and vacuum conditions of the polymerisation the volatile tetrahydrofuran is removed without contaminating the product.

The initial polymer scission probably occurs via a cyclic transition state (162). Further PBT thermal degradation then can proceed along two pathways. At higher temperatures the second reaction pathway results in the elimination of 1, 3- butadiene by concerted ester pyrolysis (163), as shown in Reaction Scheme 2.20.



Pathway 1

Pathway 2



Reaction Scheme 2.20 Thermal Decomposition of PBT (162)

This ester scission, of which 1, 3 butadiene is the main by product, limits the molar mass of the polymer obtained by melt polymerisation. Fortunately 1, 3 - butadiene volatilises without contaminating the product (163).

2.43 Uses

Thermoplastic polyesters are outstanding materials for the electrical and electronics industries, where they are used in the construction of appliances and power tools for household use. The elastomer modified grades of PBT have gained great significance in the automotive industry. The success which these materials have achieved on the market is primarily attributable to their previously described properties.

Typical applications of PBT moulding materials include:

Electrical and electronics industries:- coil formers, edge connectors, switches, distributors, fuse boxes, lamp bases and fittings, telephone and computer parts, motor components etc.

Household appliances:- infra red lamps, electric irons, toaster parts, fondue sets, hair care appliances, oven handles and buttons etc.

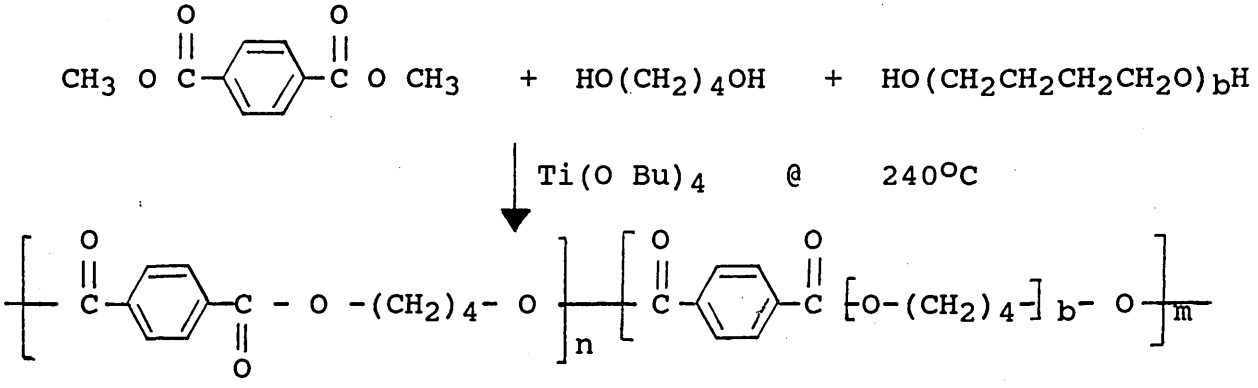
Automotive industry:- paintable bumpers, headlamp housings, window winders, ignition coil caps, rotor and distributor caps, air intakes, air filter covers, mirror parts, handles etc.

Miscellaneous uses:- wristwatch housings, friction bearings, sliding components, gears, castors cam discs and housing for vacuum pumps.

2.5 Block Copolymers Containing PBT

Literature describing thermoplastic polyester containing copolymers initially appeared during the early 1950's describing work carried out by Coleman (164). This was some of the first synthetic hetero chain block copolymer work to be performed. Coleman synthesised block copolymers containing poly(ethylene terephthalate) segments and poly(ethylene oxide) segments by the melt polycondensation of dimethyl terephthalate, ethylene glycol and hydroxyl terminated poly(ethylene oxide) in the presence of lead oxide.

Further members of the poly (alkylene terephthalate) poly(oxyalkylene) terephthalate family followed later and were conveniently prepared by the copolyesterification of dimethyl terephthalate with mixtures of short chain diol and an α, ω dihydroxy poly(oxyalkylene) (Reaction Scheme 2.21) as Coleman had initially done (165 - 167).



Reaction Scheme 2.21 Preparation of PBT Poly(oxytetramethylene) Block Copolymers (167)

Most attention has been paid to the thermoplastic elastomeric group of random PBT containing block polyetheresters. Block copolymers based on PBT as the hard block component and α, ω dihydroxy poly(oxytetramethylene) (POTM), as the soft segments, have emerged as important commercial products (168). These copolymers combine processability with excellent mechanical properties that are sustained over a wide temperature range (-55 ⟶ + 150°C), and with good resistance to many oils and chemicals. The optimum RMM of the POTM component is apporoximately 1000 and variations in the hard segment content over the range 30 - 80 wt % gives copolymers of correspondingly increasing hardness and moduli, reflecting a progressive change from soft elastomeric to tough elastoplastic character. The scientific and technological properties of these materials are discussed extensively in the literature (168 - 171).

Copolymers containing PBT and aliphatic ester blocks have been synthesised by two different routes.

(a) Coupling two preformed polyester blocks by a controlled ester-interchange reaction of two high RMM polyester homopolymers (168).

This involves the mixing of PBT and an aliphatic polyester both of high RMM at 240°C in a nitrogen atmosphere. The mixture of the two polymers changes gradually into a segmented copolymer by ester-interchange reactions.

(b) The second and alternative method for the preparation

of segmented copolyester - ester copolymers involves coupling α, ω dihydroxy aliphatic polyester and α, ω - dihydroxy PBT using diisocyanates. The blocks are probably arranged randomly, rather than in perfectly alternating sequence, since all four of the end groups on the two polyester oligomers are equally reactive with the diisocyanates. The segments of this type of block copolymer are connected by a urethane linkage. Methods of preparation and properties of diisocyanate coupled copolyesters - esters, based on PBT and produced by melt processing are mainly described in the patent literature (172 - 174).

Block copolymers of PBT and the other major thermoplastic polyester, poly(ethylene terephthalate) (PET), have been synthesised by end group coupling of pre-formed oligomers (175). The aim was to develop a faster crystallising PET which would be desirable because of its superior mechanical properties as well as its favourable economics.

Rigid block copolymers containing segments of PBT and polysulphone (11) have been obtained by the interaction of 1, 4 butane diol with terephthaloyl chloride in the presence of terephthaloyl end capped polysulphone oligomer. The butylene terephthalate compositions displayed a glass transition at 139°C and a melting transition at 200°C. The Tg value is intermediate between the Tg values of polysulphone and amorphous PBT, indicating that the amorphous fraction of the polyester and the amorphous

polysulphone were mutually soluble.

It is the aim of this thesis to present the results of experiments designed to explore new routes to the preparation of novel block copolymers of siloxane with PBT. These copolymers are anticipated to be useful as toughening agents in engineering thermoplastics.

3. SYNTHESIS AND CHARACTERISATION OF COPOLYMER PRECURSORS

3.1 Introduction

A number of linear PDMS samples of different relative molar masses, have been synthesised with a variety of functional end groups. Hydroxyl terminated PBT of several different RMM's have been obtained, and these samples have had their functional end-groups modified to give mutually reactive oligomers with the corresponding siloxane oligomer. Functionalities of the oligomers are designed such that the links between the two different segments are the hydrolytically stable Si - C link in preference to the relatively hydrolytically unstable Si - O - C.

Characterisation of the oligomers has been carried out utilising a number of analytical techniques, which include nuclear magnetic resonance spectroscopy (NMR), infra red spectroscopy (IR), high performance liquid chromatography (HPLC), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC).

In this chapter the synthetic route and subsequent characterisation of a number of mutually reactive PDMS and PBT oligomers are described.

3.2 Experimental

3.21 Characterisation Methods

3.211 General Directions

Infrared spectra were recorded using a Perkin-Elmer 783 infrared spectrophotometer. They were determined using liquid films between sodium chloride plates for siloxanes or using potassium bromide (KBr) discs for solid PBT samples.

Nuclear magnetic resonance (NMR) spectra were obtained using either a Jeol 60 MHz spectrophotometer, a Bruker WP-80 (80MHz) spectrophotometer or a Bruker AM-270 (270 MHz) spectrophotometer. For siloxane samples (unless otherwise stated) the solvent used was deuterochloroform. Tetramethyl silane (TMS) was used as an external standard, and the chemical shifts are reported using the δ scale. (TMS was used as an external standard by running just deuterochloroform with TMS as an internal standard, immediately before the siloxane sample. This is necessary due to signals at approximately 0δ associated with siloxanes). For PBT samples, deuterated trifluoroacetic acid was used with TMS as an internal standard .

Reverse phase high performance liquid chromatograpy, with water/hexafluoroisopropanol gradient, was performed on PBT samples using C18 columns and an ACS chromatography pump with a U6K injector. Detection was via a UV detector (254 nm).

The relative viscosity of PBT samples was measured as a 1%

w/w solution in m-cresol with an Ubbelohde suspended level viscometer.

Purification of Solvents.

"Analar" ether was allowed to stand over sodium wire for 24 hours before use.

Dichloromethane was allowed to stand over calcium hydride overnight before being distilled. The fraction boiling at 30 - 39°C was collected. The distillate was then stored over activated type 4A molecular sieves.

"Analar" xylene (or toluene) was allowed to stand over sodium wire for 24 hours before use.

Tetrahydrofuran was allowed to stand over calcium hydride overnight before being fractionally distilled. The fraction boiling at 63 - 67°C was collected and stored over activated type 4A molecular sieves.

Chlorobenzene was fractionally distilled and the fraction boiling at 130 - 133°C was collected and stored over 4A molecular sieves.

Dichlorobenzene was fractionally distilled and the fraction boiling at 179 -182°C collected and stored over 4A molecular sieves.

3.212 Vapour Pressure Osmometry

The number average molar masses (Mn) of siloxane oligomers were measured using a Knauer Type II vapour pressure osmometer which is normally capable of determining Mn from 50 to 20,000 g mol^{-1}. The apparatus consists of a thermostatted chamber, saturated with solvent vapour at the temperature of measurement and containing two matched

thermistors capable of detecting small temperature differences.

After calibration with a solute of known concentration, molar masses of polymers in the same solvent may be determined using the calibration and Mn can be calculated from the equation:

$$\frac{\triangle R}{c} = \frac{K}{M_n} + a_2 c$$

where $\triangle R$ = Difference in resistance

a_2 = 2nd virial coefficient

c = Solute (polymer) concentration

A calibration curve of $\triangle R/c$ vs c (mol/kg) was plotted and extrapolated to c = 0 to obtain K_{cal}. Three or four polymer solutions were prepared in the concentration range 0.02 - 0.035 molar and a plot of $\triangle R/c$ (g/kg) was extrapolated to c = 0 in order to obtain $K_{measured}$. Mn was then obtained from the ratio $K_{cal}/K_{measured}$. The experimental data are as follows.

TABLE 3.1 Experimental Details of Vapour Pressure Osmometry Measurements for PDMS Samples

Sample	Solvent	Temperature (°C)	Calibration Solute	Polymer conc. (Moles)
α,ω hydroxy-propyl PDMS (160AS)	Chloroform	37	Benzil	0.02- 0.035
α,ω hydroxy-propyl PDMS (160A)	Chloroform	37	Benzil	0.02 - 0.03

3.213 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to obtain both the number (Mn) and weight (Mw) average molar masses of polydimethylsiloxane samples. The samples were characterised using a Water Associates model GPC apparatus. The GPC technique is capable of separating polymer samples into fractions according to molecular size. This is usually achieved using a non-ionic stationary phase of packed spheres (often beads of crosslinked polystyrene) carefully produced to contain a controlled pore size distribution. The columns were calibrated by determination of elution times of previously characterised (176) standard linear PDMS samples with $Mw/Mn < 1.20$. The calibration curve for the PDMS samples covered the molar mass range $600 < Mn < 15,000$. The calibration curve is shown in Figure 3.1.

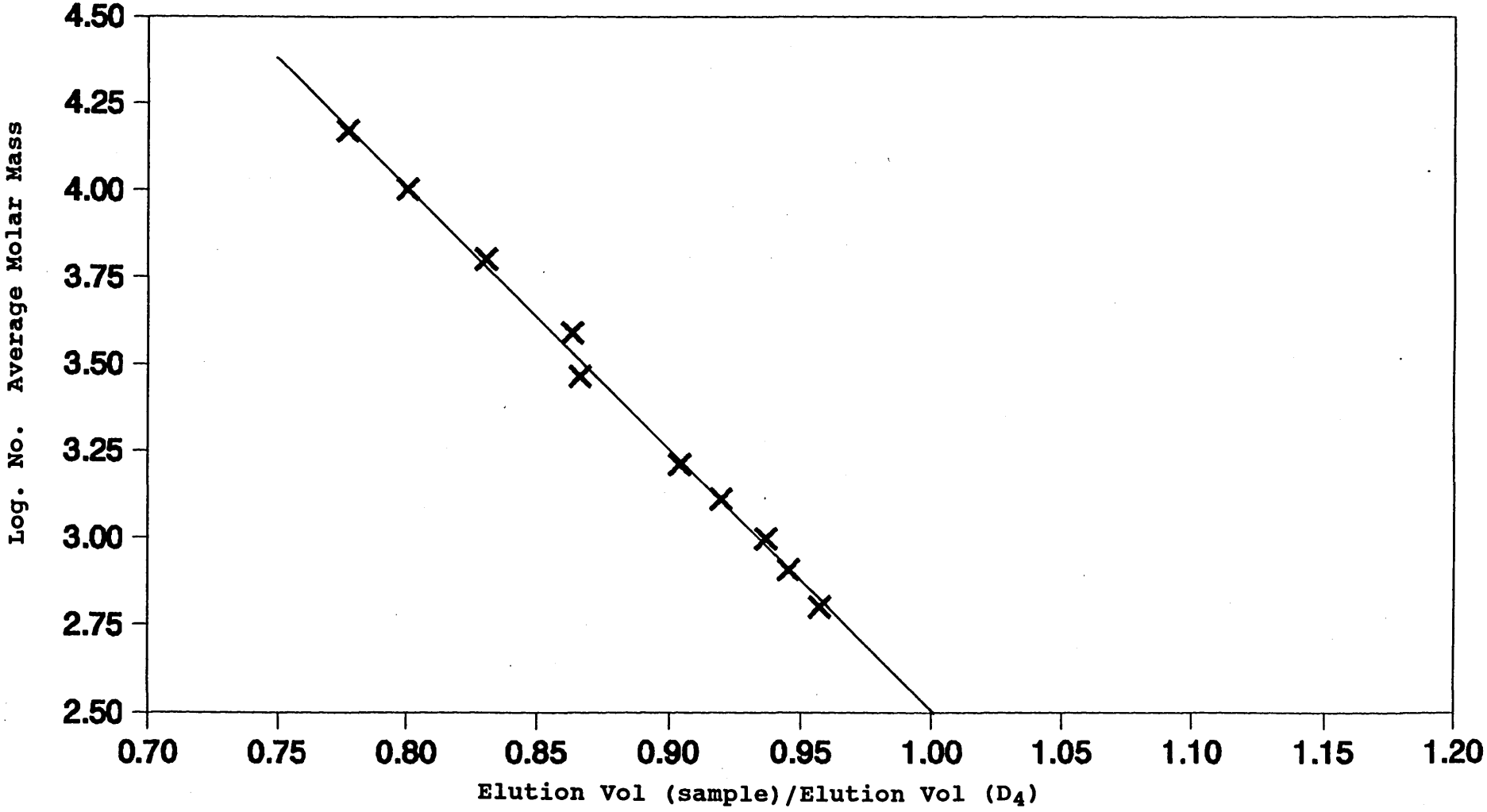


Figure 3.1 Calibration Curve For Determining Mn Of Linear PDMS Samples

In GPC calibrations the logarithm of the molar masses is plotted against the volume of solvent eluted since the injection. It is assumed that the flow rate is constant and hence the elution volume is related directly to the elution time, as recorded by the chart recorder. However, whilst the flow rate does not change appreciably over the period of time taken to elute a typical sample peak, the flow rate can and does change over longer periods of time. Hence, in this work, use was made of an oligomeric internal standard as suggested by Patel (177,178). The internal standard used in these studies was octamethylcyclotetrasiloxane (D_4).

In this work the eluted fractions were monitored by a differential refractometer and the experimental details are given in Table 3.2.

TABLE 3.2 GPC Experimental Details for PDMS Samples

Solvent	Toluene
Sample Concentration	0.5% v/v
Injection Volume	200 µl
Flow Rate	1.0 ml/min.
Columns	Porasil 60 A Bondagel E500

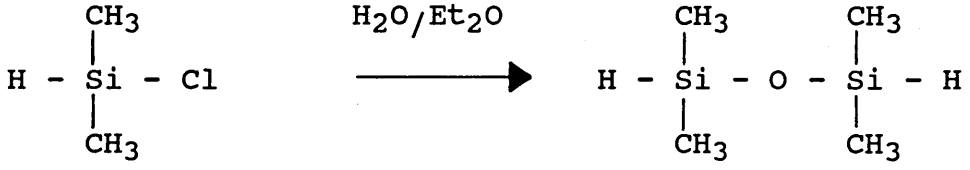
3.214 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to characterise thermal transitions of block copolymer and precursor materials.

All measurements were carried out on a Mettler DSC 30, a computer controlled instrument with a dedicated Mettler TC 10A TA processor. This allows direct calorimetric measurement, characterisation and analysis of some thermal transitions of materials. Under the control of the TC 10A TA processor, the DSC 30 is programmed from an initial to a final temperature through transitions in the sample material such as melting, glass transition and crystallisation. Data was collected at a heating rate of $10^{o}C$/min unless otherwise stated. All test pieces weighing about ~ 10 - 20mg, were sealed into aluminium sample pans.

3.22 Synthesis of Siloxane Oligomers

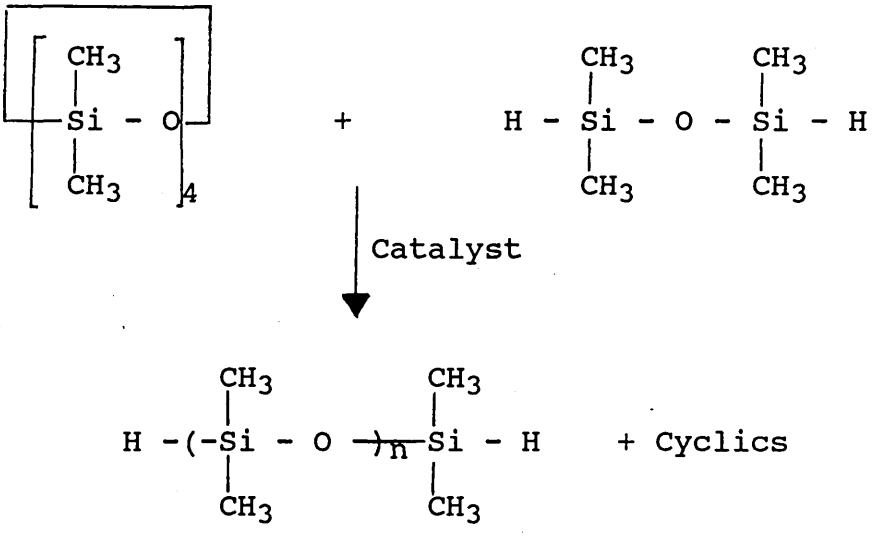
3.221 Preparation of 1, 1, 3, 3 - tetramethyldisiloxane



Reaction Scheme 3.1 Synthesis of 1,1,3,3 - Tetramethyl-disiloxane.

Dimethylchlorosilane (26g, 0.275m) was added dropwise with stirring to a mixture of ether (20ml) and crushed ice (20g). The mixture was stirred for one hour. The ether layer was separated and washed with sodium bicarbonate solution, dried over magnesium sulphate and fractionally distilled. The fraction boiling at 66°C was collected. The product was confirmed by ^1H NMR and IR analysis.

3.222 Preparation of α,ω - hydride functional PDMS oligomers



Reaction Scheme 3.2 Synthesis of Hydride Terminated Siloxane Oligomers.

Octamethylcyclotetrasiloxane (D_4) was dried over calcium hydride and redistilled before use. Tetramethyldisiloxane was used as prepared in the laboratory or as supplied by Fluka. The catalyst, acid treated Fuller's Earth, prepared when required. An outline of a typical synthesis is given below.

Cyclic tetramer (D_4) (150g, 0.507mol) tetramethyldisiloxane (10g, 0.0746mol) and catalyst (1.0g) were introduced into a dry three-necked round bottomed flask with a stirrer, thermometer and nitrogen inlet. The reaction mixture was heated under a nitrogen atmosphere at 60°C for twenty hours. After this time, the mixture was cooled and the catalyst removed by filtration through a sintered glass funnel.

The reaction mixture was then stripped of starting materials and other volatiles at 150°C under approximately 0.1 mmHg for six hours. The final product was subjected to ^1H NMR, I.R. and GPC analysis.

3.223 Protection of 10 - Undecenoic Acid

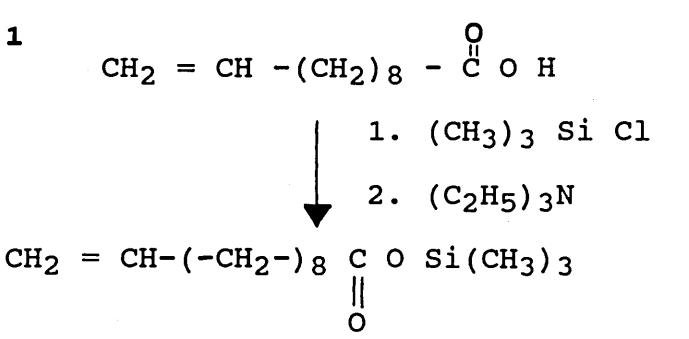
10 - Undecenoic acid was distilled before use (110°C at 0.2 mmHg). Trimethylchlorosilane (54.47g, 0.5m 10% xs) in dry dichloromethane (40ml) was added to a solution of undecenoic acid (84g, 0.456m) in dry dichloromethane (30ml) and the reaction mixture refluxed for four hours. A solution of triethylamine (50.6g, 0.5m) in dry dichloromethane was then added with care when the reaction mixture had cooled. Then the reaction mixture was refluxed for a further sixteen hours, during which the reaction mixture was monitored (by I.R.) to ensure that no carboxylic acid groups remained.

Once cool the triethylamine hydrochloride formed was removed by vacuum filtration under nitrogen and the dichloromethane by rotary evaporation. The crude product was redissolved in petroleum spirits, since triethylamine hydrochloride is sparingly soluble in dichloromethane. The remaining triethylamine hydrochloride was removed and the petroleum spirits removed by rotary evaporation. The product was isolated by vacuum distillation. A clear liquid distilling over at 72°C at 3mmHg. The product was confirmed using I.R. and ^{1}H NMR.

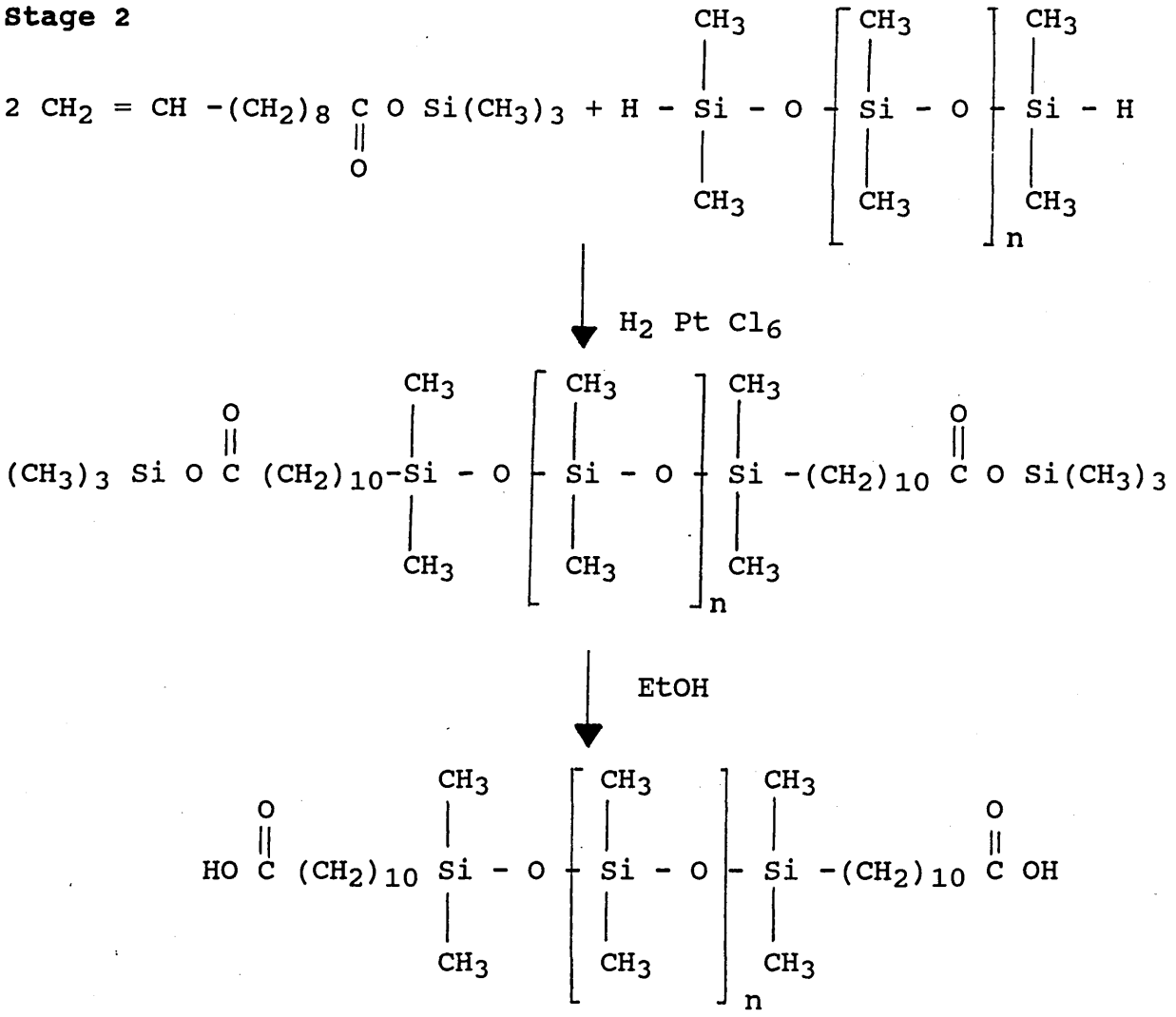
3.224 Preparation of α,ω carboxydecyl PDMS

A typical procedure is outlined below, and shown in Reaction Scheme 3.3. A mixture of α,ω di(hydrosilane) PDMS (20g, 0.01m), dry xylene (80ml), trimethylsilyl ester of 10 - undecenoic acid (16.71g, 0.06m) and chloroplatinic acid (4.4 ml, 2.28 $x10^{-5}$m in dry tetrahydrofuran) was heated under reflux for eighteen hours in a three-necked light sealed round bottomed flask. The reaction was monitored by the disappearance of the Si - H (I.R. 2120 cm^{-1}) signal. Ethanol (20ml) was added and the reaction mixture was then heated for a further hour to effect hydrolysis of the trimethylsilyl ester groups. The residue was taken up in ether (75ml) after evaporation to dryness and the chloroplatinic acid residues were extracted with water. The ether was dried and evaporated to give the required polymer and residual excess undecenoic acid. The undecenoic acid was removed by dissolving the crude product

Stage 1



Stage 2

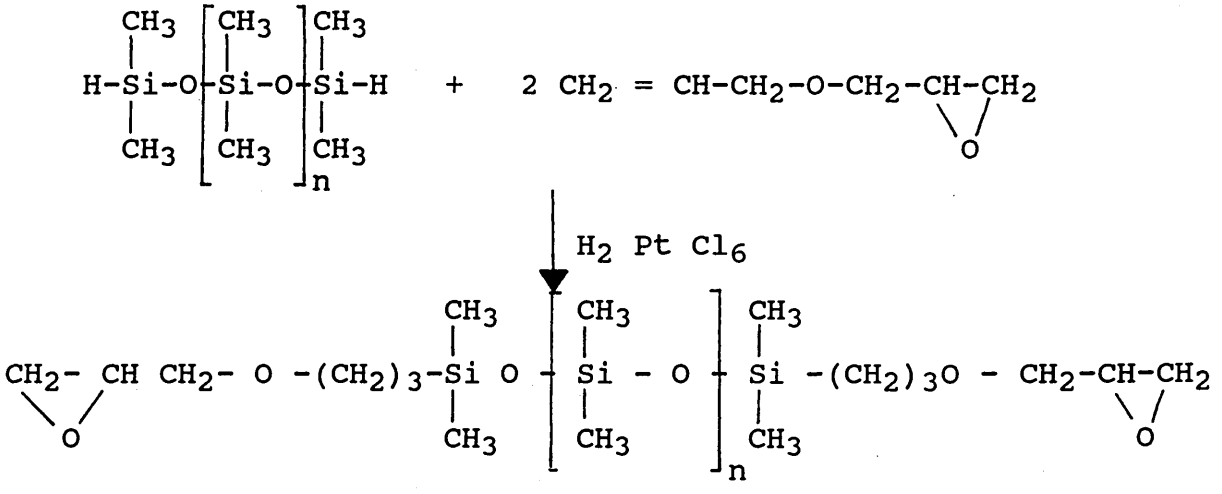


Reaction Scheme 3.3 Preparation of α,ω Carboxydecyl PDMS

in acetone and then adding 15% v/v of water to the mixture causing the polymer to precipitate out. The product was confirmed by ^1H NMR and I.R.

3.225 Preparation of α,ω Diepoxy Oligosiloxanes

A mixture of 1- Allyloxy 2, 3 - Epoxypropane (AEP) (2.51g, 0.022 moles) and chloroplatinic acid (2.135×10^{-5}moles in dry THF) was added to a light sealed three-necked round bottomed flask fitted with dropping funnel, stirrer, condenser and nitrogen inlet. A solution of α, ω - di(hydrosilane) PDMS (20g, 0.01moles) in petroleum ether was added dropwise to the mixture. This was then heated to 50°C and retained at this temperature for two hours. The reaction mixture was then refluxed for twelve hours. Excess AEP was then removed by vacuum distillation at 150°C for three hours. The product was then analysed by ^1H NMR and I.R.

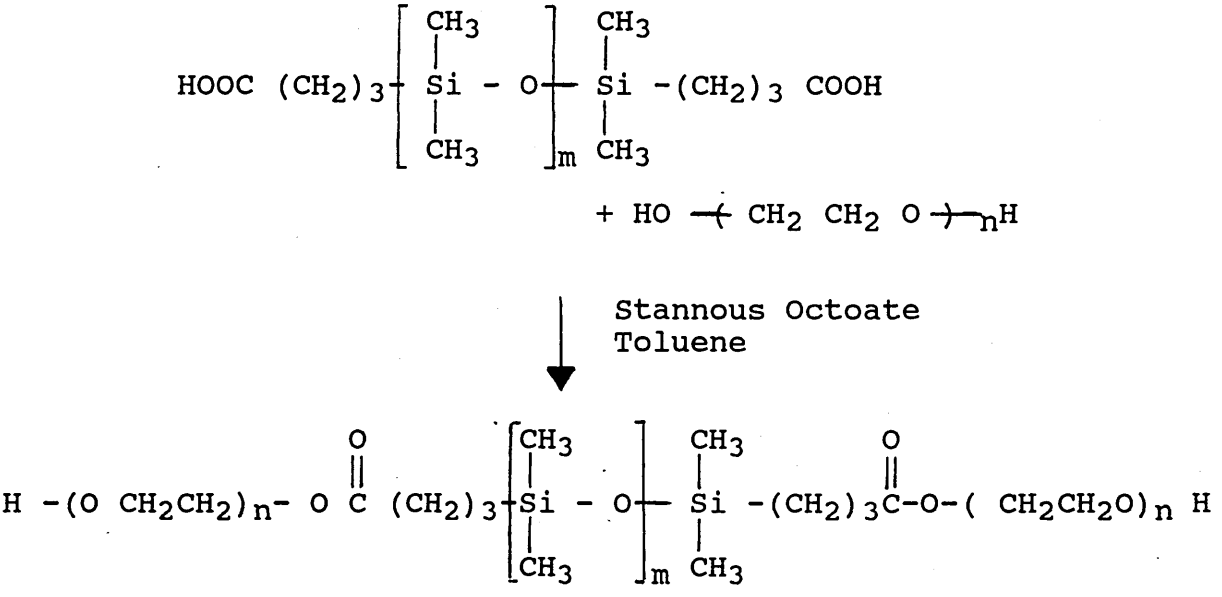


Reaction Scheme 3.4 Synthesis of α,ω -diepoxy oligosiloxanes

3.226 Reaction of Trimethylsilylallyl amine with α,ω di(hydrosilane) PDMS

Trimethylsilylallyl amine was used as supplied (by Petrach). A mixture of α,ω di(hydrosilane) PDMS (5g, 2.5 x 10^{-3} moles), trimethylsilylallyl amine (3.23g, 2.5 x10^{-2} moles) and hexachloroplatinic acid (3.85 x 10^{-5} moles in dry THF) in dry xylene was heated at 80°C for ninety six hours, removing samples every twelve hours to monitor disappearance of Si - H groups (I .R.).

3.227 Synthesis of Poly(ethylene glycol) terminated PDMS



Reaction Scheme 3.5 Preparation of poly(ethylene glycol) Terminated PDMS oligomers

A solution of α,ω - carboxypropyl PDMS (10g, 0.01 moles) in dry toluene (20ml) was slowly added to a stirred solution of poly(ethylene glycol) (4.2g, 0.021 moles) in dry toluene (20ml) together with a catalytic amount of stannous octoate (2,000ppm with relation to siloxane i.e. 20mg).

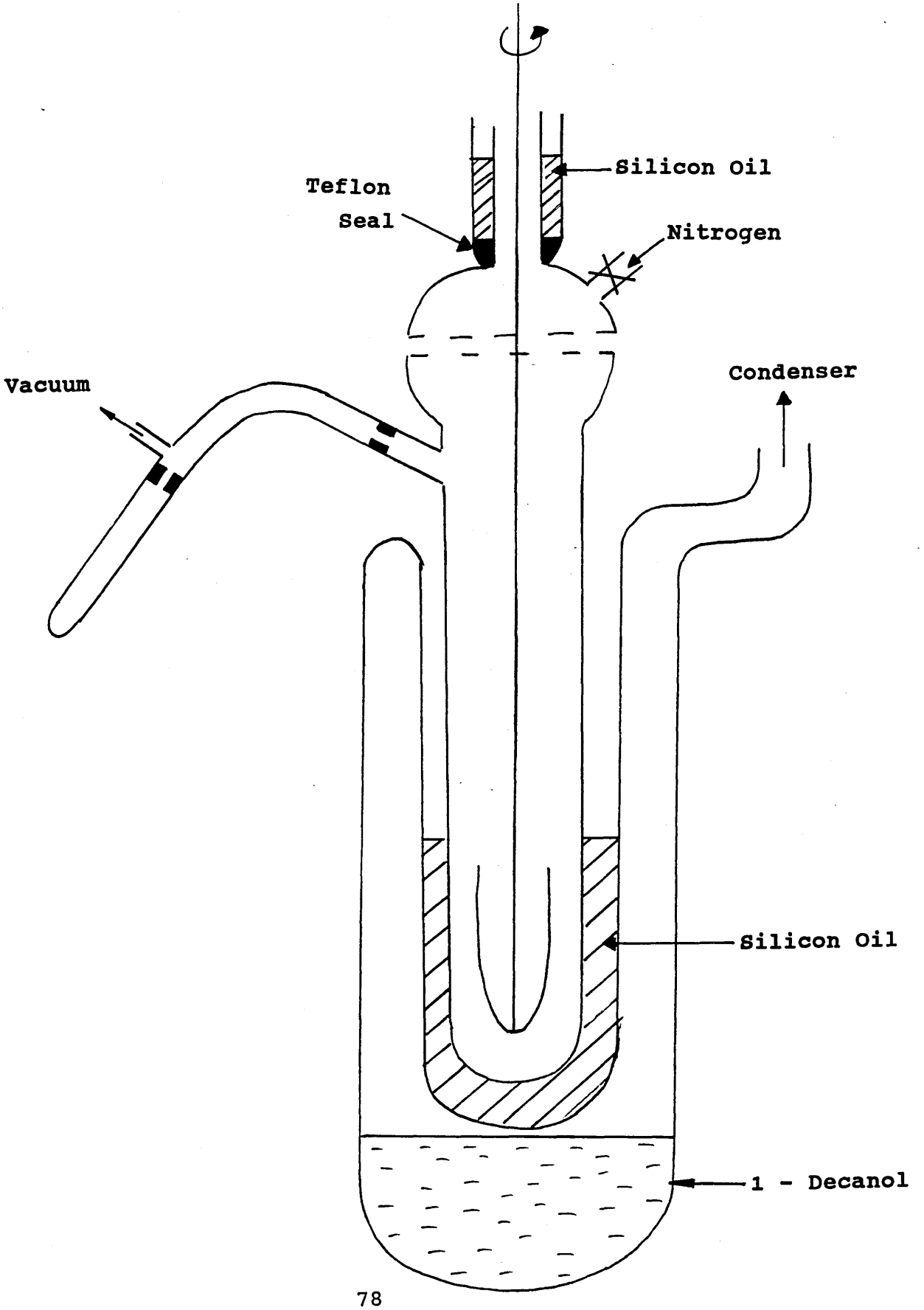
The mixture was then refluxed for twenty four hours with the water produced being removed by the aid of a Dean-Stark trap. The excess toluene was removed by rotary evaporation. ^1H NMR and the I.R. spectrum of the product were recorded.

3.23 Synthesis of Poly(butylene terephthalate) (PBT) Oligomers

3.231 Preparation of α,ω - hydroxy terminated PBT

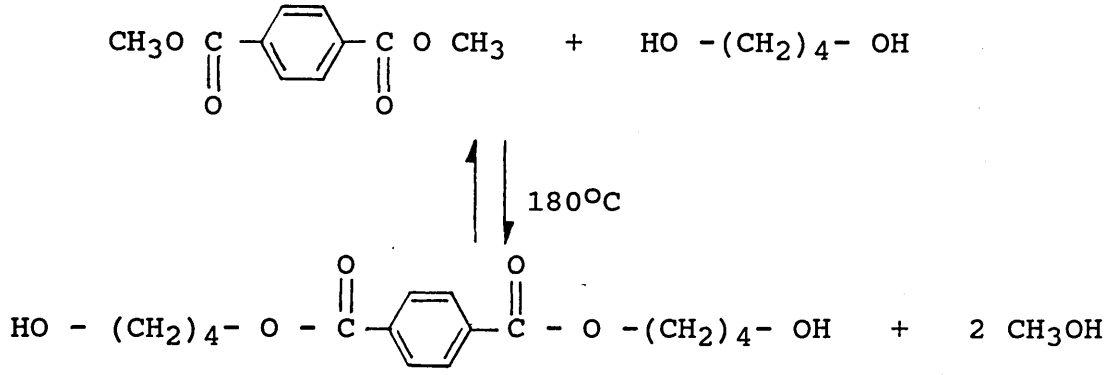
Dimethylterephthalate (20g, 0.103 moles), 1, 4 Butane diol (13.15g, 0.134 moles) and tetraisobutyltitanate (40mg) were added to a polymer tube bearing a side arm, (see Fig.3.2). The tube was partially immersed in a 180°C vapour bath to melt the mixture. The reaction mixture was stirred under a nitrogen atmosphere for approximately one hour, during which methanol was distilled from the mixture. The system was then evacuated (to 20mmHg in thirty minutes) to remove final traces of methanol. The polymerisation tube was now heated by means of a 230°C vapour bath (n - decanol).

The pressure was reduced to 0.1 mmHg in approximately fifteen minutes. The polymerisation was continued for two hours, before filling the flask with nitrogen and removing the sample. Larger samples of PBT of different relative molar masses were prepared at Akzo. These samples were characterised by ^1H NMR, I.R., DSC, HPLC and relative

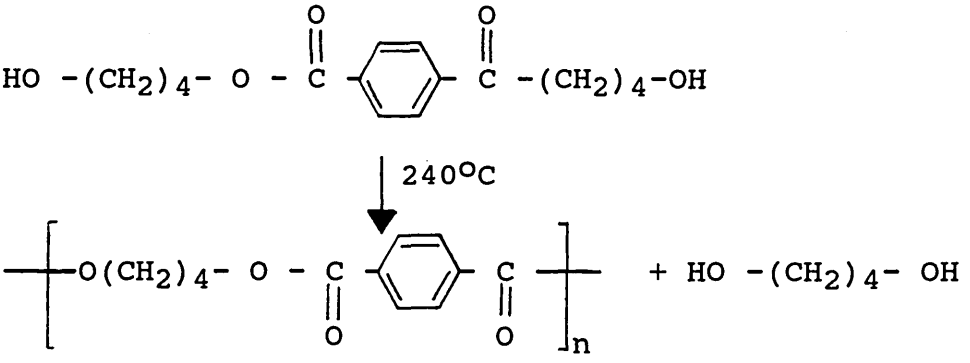

Teflon
Seal
Silicon Oil
Nitrogen
Vacuum
Condenser
Silicon Oil
1 - Decanol

viscosities, details of which appear in Table 3.6.

Step 1 Ester Interchange



Step 2 Polycondensation



Reaction Scheme 3.6 Synthesis of α,ω - hydroxy PBT Oligomers

3.24 Vinyl Functionalisation of PBT Oligomers by Solution Methods

3.241 Reaction of α,ω hydroxy PBT Oligomers with Acryloyl Chloride

α, ω hydroxy PBT (2.8984g, 2.4×10^{-3} moles) was added to chlorobenzene (30mls) and refluxed. A solution of acryloyl chloride (4.302g, 4.8×10^{-2} moles) in chlorobenzene (25mls) was then added dropwise with care.

After fifteen minutes a solution of triethylamine (4.345g, 4.3×10^{-2} moles) in chlorbenzene (~ 30 mls) was added slowly, dropwise, to the reaction mixture and allowed to reflux for a further one hundred hours.

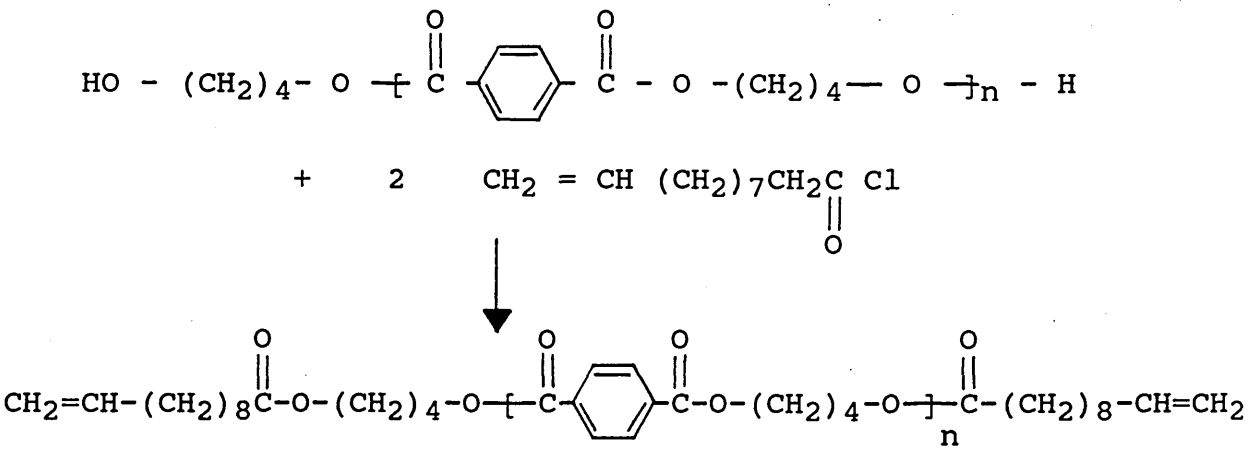
On cooling some material precipitated out. This was collected by filtration, washed with water and dried in the vacuum oven at 110°C. This was subjected to ^1H NMR and I.R. analysis. Some material had become soluble in the chlorobenzene and this was analysed by ^1H NMR once the chlorobenzene had been removed by rotary evaporation.

3.242 Reaction of α,ω hydroxy PBT Oligomers with Acrylic Acid

PBT (2.5840g, 2.13 x 10^{-3} moles) was placed in a two necked flask fitted with condenser and Dean-Stark trap. A N-methyl pyrrolidone (NMP), toluene mixture (66.7/33.3 v/v) (~ 40 mls) was added to the flask. Acrylic acid (3.06g, 4.25 x 10^{-2} moles) was added together with p-toluene sulphonic acid (0.1g).

The reaction was refluxed for forty eight hours. On cooling precipitated material was removed by filtration. The remaining product was obtained by adding a large excess of non-solvent (methanol). The product was isolated by filtration, dried under vacuum and then analysed by ^1H NMR and I.R.

3.243 Reaction of α,ω - hydroxy PBT Oligomer with 10-Undecenoyl Chloride



Reaction Scheme 3.7 Reaction of α,ω - hydroxy PBT Oligomer with 10 Undecenoyl Chloride

PBT (2.461g, 2 x 10^{-3} moles) was placed in a three-necked round bottomed flask equipped with a dropping funnel, condenser and nitrogen inlet. N - methyl pyrrolidone (NMP) (30mls) was then added. A solution of 10 - undecenoyl chloride (0.9122g, 4.4 x 10^{-3} moles) in NMP (10mls) was added to a dropping funnel.

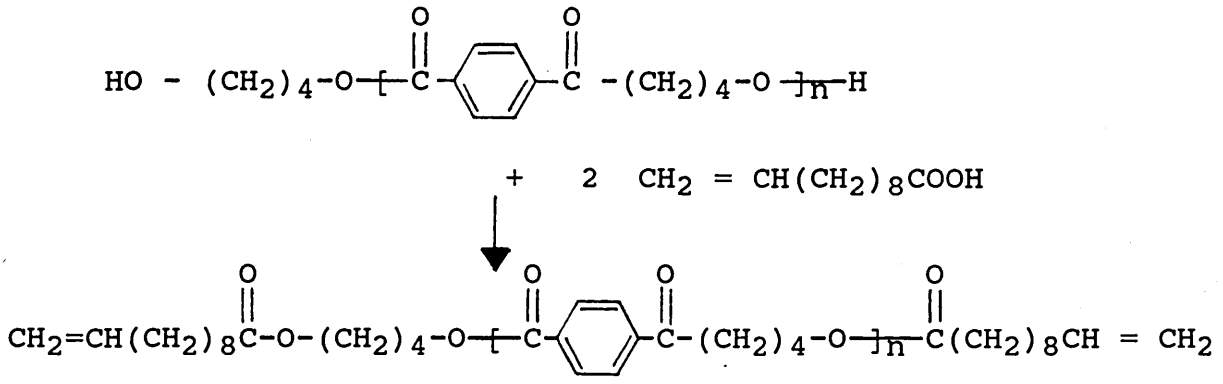
The PBT mixture was heated until it became solvated (approx. 130°C) and the acid chloride solution was added slowly dropwise. Once the acid chloride mixture had been added the reaction mixture was maintained for sixteen hours at 150°C.

The reaction mixture was then cooled and precipitated material filtered. However, some material had become soluble and this was recovered by precipitation by adding the reaction mixture to a large excess of methanol. Most

of the excess methanol was removed by decantation and the product was collect by filtration. The product was then dried in the vacuum oven for three hours and analysed by I.R. and ^1H NMR.

3.25 Vinyl Termination of α,ω - hydroxy PBT Oligomer by Melt Techniques

3.251 Reaction of α,ω - hydroxy PBT with 10 - Undecenoic Acid



Reaction Scheme 3.8 Reaction of α,ω - hydroxy PBT Oligomers with 10-Undecenoic acid

PBT (40g, 0.0329 moles) which had been dried overnight in a vacuum oven was added to the reaction vessel (see Fig. 3.2). This was immersed in a silicon oil bath at 230°C. Once the PBT was molten, 3-4 drops of triethyleneglycol phosphoric acid (TEGPA) was added to the PBT. This mixture was then stirred for 30 minutes under nitrogen. Then 10-undecenoic acid (14.81g,0.08 moles) was added slowly to the reaction vessel. The stirrer speed was accelerated to facilitate mixing and once a homogenous mixture was observed, it was returned to its original speed. The reaction was carried out for a further two hours. Samples were removed at time intervals. I.R. spectra of each of

the samples and the final product were recorded. GPC and ^1H NMR analyses were carried out on the final product.

3.252 Optimisation of Catalytic Species for Vinyl Functionalisation of PBT

A number of vinyl terminated PBT samples were prepared using a variety of catalysts. A typical procedure is given below.

α,ω - hydroxy PBT (30g, 1.87×10^{-2} moles) was dried under vacuum at 130°C for sixteen hours. PBT was added to the reaction vessel and melted under a nitrogen atmosphere. TEGPA (~ 2000ppm) was added to the molten PBT and the mixture stirred for thirty minutes. Undecenoic acid (7.24g, 3.93×10^{-2} moles) was added together with the catalyst and the stirrer speed increased for two minutes to ensure complete mixing. After two hours a vacuum (~ 5mmHg) was applied for forty five minutes, after which the reaction was stopped. The products were subjected to I.R., ^1H NMR and DSC analysis.

Four catalysts were compared for the synthesis of vinyl terminated PBT. Details of the catalyst species utilised are given below, (see Table 3.3).

TABLE 3.3 Catalysts used in the Synthesis of α,ω Vinyl Terminated PBT

Sample	Catalyst
RK901 / 01	TEGPA added to deactivate titanate
RK901 / 02	p - toluene sulphonic acid
RK101 / 01	Titanate present in PBT
RK101 / 02	Stannous octoate
RK101 / 03	TEGPA added to deactivate titanate

RK901 α,ω hydroxy PBT RMM = 1215

RK101 α,ω hydroxy PBT RMM = 1604

3.253 Reaction of α,ω hydroxy PBT with 10-Undecenoyl Chloride

PBT (40g, 0.0329 moles) was melted and then, TEGPA (~ 2000 ppm) was added and the mixture stirred for thirty minutes. 10 - undecenoyl chloride (15.01g, 0.074 moles) was added and the reaction mixture stirred for a further twenty minutes before being terminated. The final product was subjected to I.R. and ^1H NMR and GPC analysis.

3.3 Results and Discussion

3.31 Synthesis of Siloxane Oligomers

α, ω di(hydrosilane) PDMS is a main precursor to functionalised siloxanes and is synthesised by the cationic polymerisation of D_4 in the presence of tetramethyl disiloxane (61).

Tetramethyl disiloxane (an end blocker in the preparation of α, ω di(hydrosilane) PDMS) was obtained by the co-hydrolysis of dimethylchlorosilane. An I.R. spectrum of the clear liquid product contained the stretching frequencies expected (179), namely 2120 cm^{-1} (Si - H), 1040 - 1050 (Si - O - Si), 1260 (Si - CH_3). ^1H NMR further confirmed the expected product with a multiplet at 4.60 δ and a doublet at 0.1δ, with integral step height ratios corresponding to two and twelve hydrogens respectively.

Synthesis of α,ω di(hydrosilane) PDMS oligomers was carried out according to a number of cationic methods (90,91,93,180) in which both the catalyst and ratio of D_4 to end blocker were varied. Catalysts investigated included concentrated sulphuric acid, trifluoroacetic acid and acid activated Fuller's earth, since it may be easily removed by filtration. Fuller's earth was therefore chosen as the catalytic species. This ring opening polymerisation technique is known as an equilibration or redistribution reaction. During the reaction the catalyst can cleave Si - O bonds in cyclic or linear species including that of the

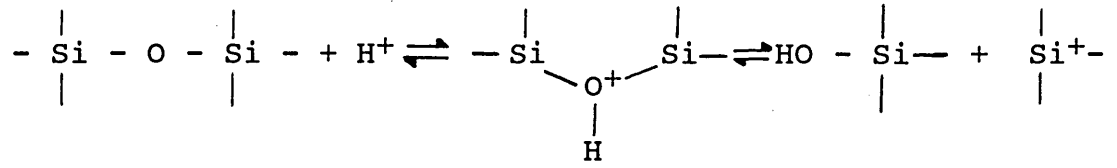
"end blocker". However, the Si - H bonds are stable. Thus at the end of reaction the linear oligomers are functionally terminated with - Si - H groups and the minority of (10 - 15%) cyclic side products are non-functional. After elimination of the catalyst the cyclic side products are usually removed from the system by vacuum distillation at elevated temperatures. The number average molecular mass of the final product is determined by the initial ratio of cyclic monomers to the end blocker.

TABLE 3.4 Synthesis of α,ω di(hydrosilane) PDMS Oligomers

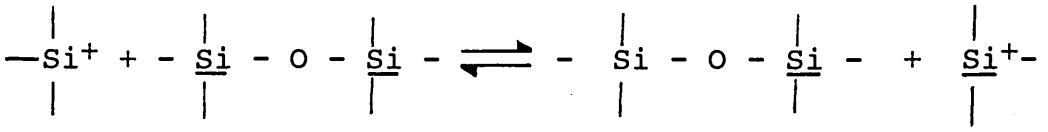
Sample	D_4 (g)	End Blocker (g)	Mn g/mole Theoretical	Mn Obtained GPC	Mw/Mn
1	150	10	2144	1172	2.18
2	150	15	1474	893	1.94
3	150	30	804	608	1.27

Table 3.4 provides a summary of the experimental data and the results obtained. As expected number average molar mass values are lower than theoretical. This is probably due to the random nature of the equilibration reaction together with the formation of cyclic side products. Mn was obtained by equating the peak molar mass, Mpk, with $(MwMn)^{1/2}$ as done by Kendrick (69) for a series of sharp fractions of PDMS. Further work (176) confirmed that Mpk was closest to $(MwMn)^{1/2}$ in a study of three different calibrations i.e. Mpk = Mn, Mpk = Mw and Mpk = $(MwMn)^{1/2}$.

However, with a redistribution reaction there is a potential problem, both linear and cyclic siloxane species undergo redistribution. The process is based on the cleavage of Si - O - Si bonds in the siloxane backbone. It is this susceptibility of the Si - O - Si linkages in linear siloxanes to undergo scission and bond reformation, by the action of strong acids (Reaction scheme 3.9) and strong bases, that creates the following problems.



INITATION



CHAIN GROWTH

Reaction Scheme 3.9 Redistribution of Siloxanes by Acidic Catalysis

These processes can lead to a randomisation of siloxane units between polysiloxane chains and hence to a broadened distribution of RMM's in the presence of strong acids or bases.

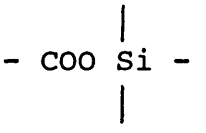
Therefore care has to be taken when attempting to functionalise siloxane oligomers utilising protected molecules. This is because classical chemical deprotection methods (181) involve the use of strong acids or bases, which cannot be used here.

α, ω - carboxy functionalised PDMS oligomers offer the

possibility of reaction with α, ω hydroxy PBT to form the desired block copolymers. 10 - undecenoic acid was chosen since it could theoretically be attached to α, ω di(hydrosilane) PDMS, via hydrosilation, and in the process form the hydrolytically stable Si - C linkage.

Two further advantages of utilising undecenoic acid are that its boiling point (~310°C) is above the process temperature of PBT, with which it has been shown to react successfully in the melt and the long alkyl chain may increase the siloxanes compatibility towards the PBT.

However, before attaching undecenoic acid to PDMS, the carboxyl group must be protected since Si - H groups react when heated in the presence of carboxyl groups to give silylated derivatives (182).



The carboxyl groups were protected by a trimethyl silyl group, which is easily removed by boiling alcohol. Silation of the carboxylic acid group is achieved in approximately 70% conversion.

The attachment of protected undecenoic acid to α, ω di(hydrosilane) PDMS was performed by hydrosilation using a three fold excess of the acid. The reaction was monitored by I.R. observing the disappearance of the Si - H signal (Figs. 3.3 and 3.4). The signal had disappeared after eighteen hours.

The deprotection of undecenoic acid, once attached, was carried out using boiling ethanol. After rotary evaporation the crude material contained the desired end product and excess undecenoic acid. The excess undecenoic acid was removed by adding the crude matrial to an acetone/water (85/15) mixture, in which the undecenoic acid disolves while the acid functionalised PDMS precipitates out (183).

The product obtained from the precipation was characterised by ^1H NMR and I.R.. The ^1H NMR (Fig. 3.5) shows a signal at 0δ which is due to Si - CH_3 groups also a small multiplet signal at 1.2δ which is due to methylene protons in the alkyl chain of the polymer. There is no significant evidence of vinyl protons or the Si - H signal. The I.R. spectrum (Fig. 3.6) shows a broad signal between 3300 cm^{-1} - 2500cm^{-1} which is characteristic of carboxylic acid groups. The signals at 1260 cm^{-1}, 1100 - 1000 cm^{-1} and 800 cm^{-1} are characteristic of siloxanes. In the I.R. spectrum there are no signals characteristic of Si - H or - $CH=CH_2$ groups. This evidence indicates that the acid

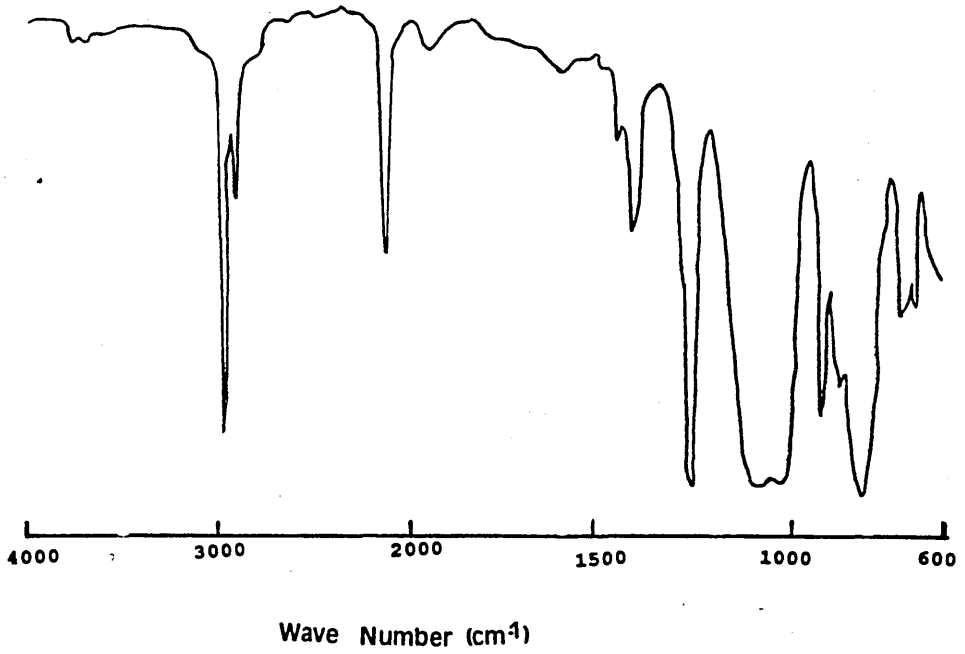


Figure 3.3 I.R. Spectrum Of α,ω Di(hydrosilane) PDMS

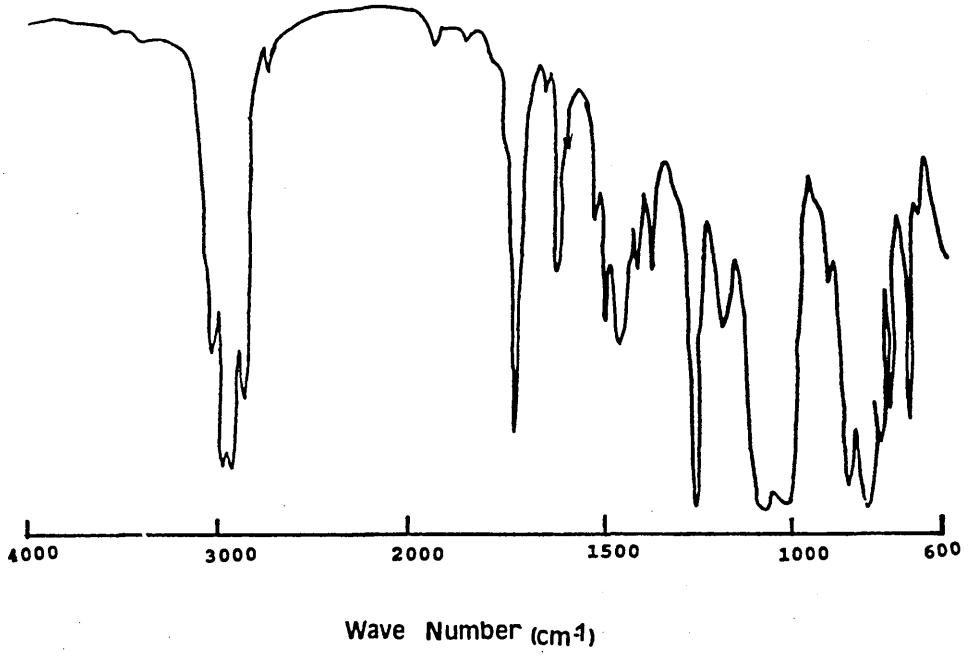
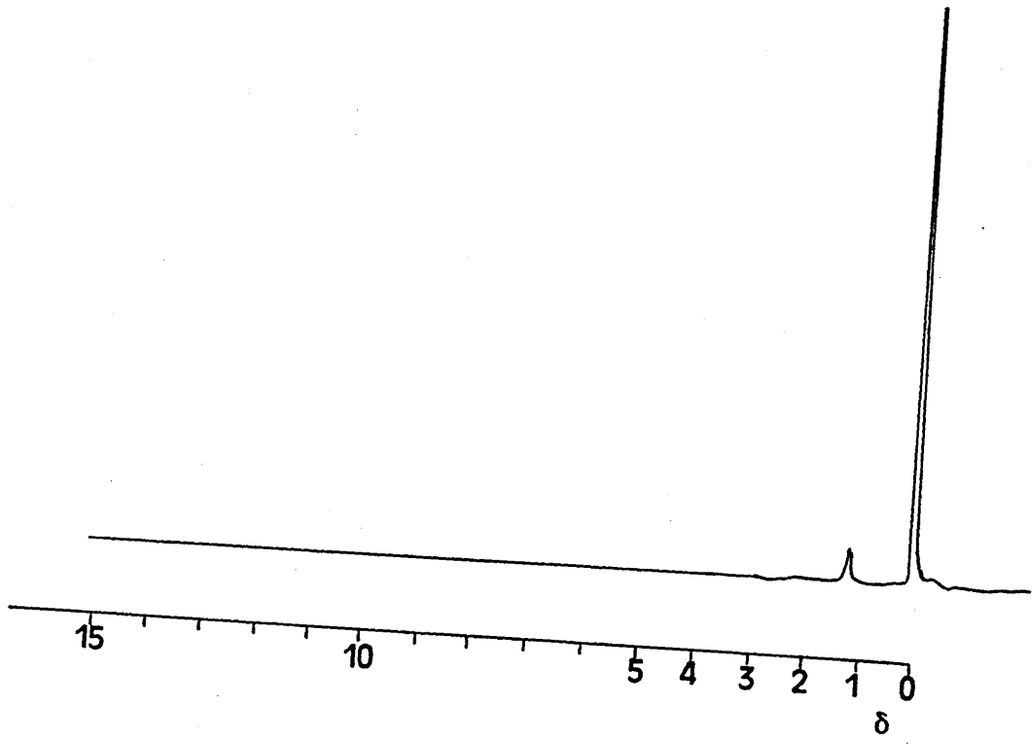


Figure 3.4 I.R. Spectrum Of Reaction Product of α,ω Di(hydrosilane) PDMS With Trimethylsilylester Of Undecenoic Acid

Figure 3.5 ^{1}H NMR Spectrum Of α,ω Bis(10 Carboxydecyl) PDMS



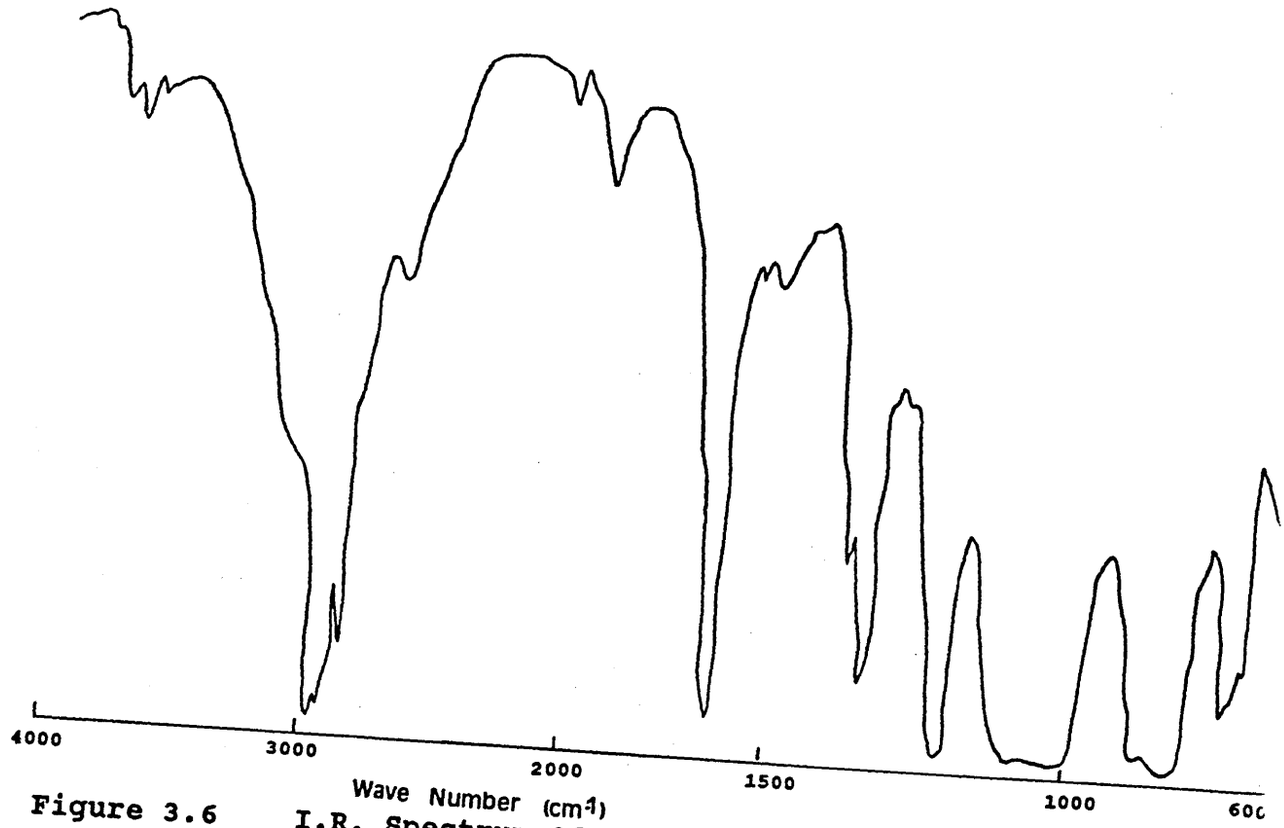
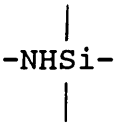


Figure 3.6 I.R. Spectrum Of α,ω Bis (10 Carboxydecyl) PDMS

functionalisation of PDMS was successful.

Amine terminated siloxane oligomers are a potential precursor to block copolymer formation with PBT, since the two can be linked by a transamidation reaction (184). The route chosen to synthesise the amine functionalised oligomer was very similar to that of the acid material i.e. hydrosilation reaction of α,ω di(hydrosilane) PDMS with a silyl protected allylamine. Protection of the amine is required as it too can react with Si - H groups when heated to yield silylated derivatives (182).



Unfortunately the reaction proved unsuccessful. The Si- H signal remained even after long reaction times of up to seven days. Catalyst effectiveness was checked, vast excesses (10x) of protected amine were used and also greater amounts of catalyst, in conjuction with long reaction times were attempted. However, the Si - H groups remained unreacted.

An explanation for these observations is that the catalyst could be poisoned by one of the reactants, rendering it inactive. Platinum catalysts are susceptible to poisoning by many things (125), especially good donors. Hexachloroplatinic acid has weakly attracted ligands associated with it in it's initial form. These are easily displaced by an alkene, which becomes co-ordinated and

subsequently activated. Co-ordinated alkenes are known to show enhanced susceptibility to attack by nucleophiles (126), such as H^- derived from Si - H cleavage.

However, the nitrogen present in the protected amine is possibly a good donor and could interact strongly with the platinum catalyst. As this new ligand is not easily removed, further alkene could not be co-ordinated and hence the reaction prevented. Possible evidence for this is only an initial decrease in the intensity of the I.R. Si - H signal.

Siloxanes functionalised with terminal epoxy groups have the potential to react with either hydroxyl or carboxylic acid functionalised terminated PBT. α, ω diepoxysiloxanes were prepared in reasonably high yields by the hydrosilation reaction between 1 - Allyloxy 2,3 epoxypropane and α, ω di(hydrosilane) PDMS. The I.R. spectrum of the reaction product exhibits the following characteristics :

(i) Complete disappearance of the Si - H (2120 cm^{-1}) signal and the C = C (1645 cm^{-1}) signal.

(ii) Appearance of the two bonds characteristic of epoxy groups (850 and 920 cm^{-1}).

Further evidence of the success of the reaction was given by the disappearance of the Si - H group in the ^1H NMR spectrum, lack of multiplet at 4.6δ and the emergence of signals assigned to epoxy protons (2.5 - 3.5δ).

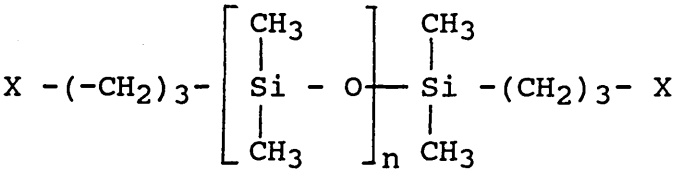
α, ω carboxy-propyl terminated PDMS oligomers were reacted with low molar mass hydroxyl terminated poly(ethylene glycol) (PEG) to produce PEG capped PDMS oligomers. The purpose of this was to use the product to form segmented copolymers in a similar manner to the commercially available polyether - polyester copolymers. These are produced by the reaction between ethylene glycol capped poly(oxypropylene) and PBT (168).

Spectroscopic evidence (I.R. and ^1H NMR) gave strong evidence of the success of the reaction, i.e. the disappearance of the broad carboxyl peak (3300 cm^{-1} - 2500 cm^{-1}) in the I.R. spectrum, together with the lack of carboxyl signal at approximately 11.8δ in the ^1H NMR. It is expected that the presence of the polyether groups will make the siloxane more compatible in melt phase reactions to form a block copolymer.

TABLE 3.5 Characterisation Data of Commercially Supplied Functional Siloxanes

Sample	End Group Functionality	RMM
160 A	- OH	960[a]
160 AS	- OH	1940[a]
KF 101	$-CH_2-CH(O)-CH_2$	700[b]
161 A	$-NH_2$	1680[b]
TEGO 2010	$-NH_2$	1040[b]
TEGO 2140	- COOH	1100[b]
VP 1085	- H	1910[c]

General Structure.



Characterisation Method.

(a) VPO

(b) Manufacturers data

(c) ^1H NMR

3.32 Synthesis of Functionalised PBT Oligomers

3.321 α,ω Hydroxy Terminated PBT

The step growth polymerisation process is used to prepare a wide range of commercially important polymers, such as PBT. Chain growth occurs by condensation reactions between functional groups in bifunctional monomers.

Polyesterifications are examples of a step growth system and are characterised by the polycondensation reaction of a diol and dicarboxylic acid or an ester exchange between a diol and a diester. The latter case was utilised in this work. In the preparation of PBT, dimethylterephthalate and 1,4 butane diol were used.

Standard commercial grade PBT (supplied by Akzo), has an average degree of polymerisation of approximately 100 and a corresponding molar mass of 22,000. Lower molar mass materials may be synthesised by using a precisely controlled stoichiometric imbalance of the reactants. For example, an excess of butane diol over dimethylterephthalate would eventually produce PBT with two hydroxyl end groups incapable of further growth when the dimethylterephthalate is totally consumed.

The number average chain length x_n of the low molar mass materials may be calculated using the Carothers equation (185):

$$x_n = \frac{1 + r}{1 + r - 2rp}$$

where

r is the ratio of the number of molecules of reactants.

p is the extent of reaction.

Therefore given a required molar mass the required ratio of the two difunctional monomers to each other can be determined. For high molar mass polymers, highly purified monomers are needed since the extent of reaction (p) must be as close to one as possible. Small deviations detract from the theoretical molar mass significantly.

Hydroxyl functionalised PBT samples with theoretical molar masses of 500, 1000, 2000, 5000, and 10,000 were synthesised by utilising a stoichiometric imbalance of the coreactants. However, owing to the random nature of polyesterifications, observed molar masses deviated slightly from those expected (see table 3.6).

RK 901 and 101 were synthesised by a direct esterification of dimethylterephthalate (DMT) with 1, 4 butane diol (BD) with BD/DMT ratio's of 1.5 and 1.25 respectively. Theoretically this should give oligomers with RMM = 530 and 970 respectively.

TABLE 3.6 Characteristics of Low Molar Mass PBT Samples

Code	n rel[a]	end groups (meq/Kg) [b]				RMM
		e_{OH}	e_C	e_M	e_{tot}	
RK 901	1.069	1540	11. 8	94.5	1646	1215
RK 101	1.119	1075	67	165	1247	1604
RK 123	1.187	723	7.15	2.1	732	2732
RK 131	1.362	310	17. 5	0.65	328	6097
RK 143	1.838	115	29. 1	0.5	145	13793

(a) n rel = "relative viscosity", measured as a 1% w/w solution in m - cresol.

(b) e_{OH}, e_C, e_M, e_{tot}, = hydroxyl(186), carboxyl(187), methylester(188), total end group concentration.

A further sample of PBT (A8 3102) of low RMM (2,000) was supplied at a later date.

RK 123, 131 and 143 were made by esterfication of DMT and BD (BD/DMT = 1.5), followed by a short polycondensation step (i.e. vacuum 0.05 - 0.1 mm Hg and higher temperature ~ 230°C). The polycondensation time period governs the extent of degree of polymerisation. In all cases tetrabutyltitanate was used as a catalyst.

HPLC analysis of the lower molar mass species (i.e. RK 901 and 101) gives a multiplicity of peaks, indicating the many different oligomeric species present in the reaction product (Fig. 3.7). This is to be expected for oligomeric polycondensation products, leading to broad RMM distributions. In the PBT samples that have undergone a

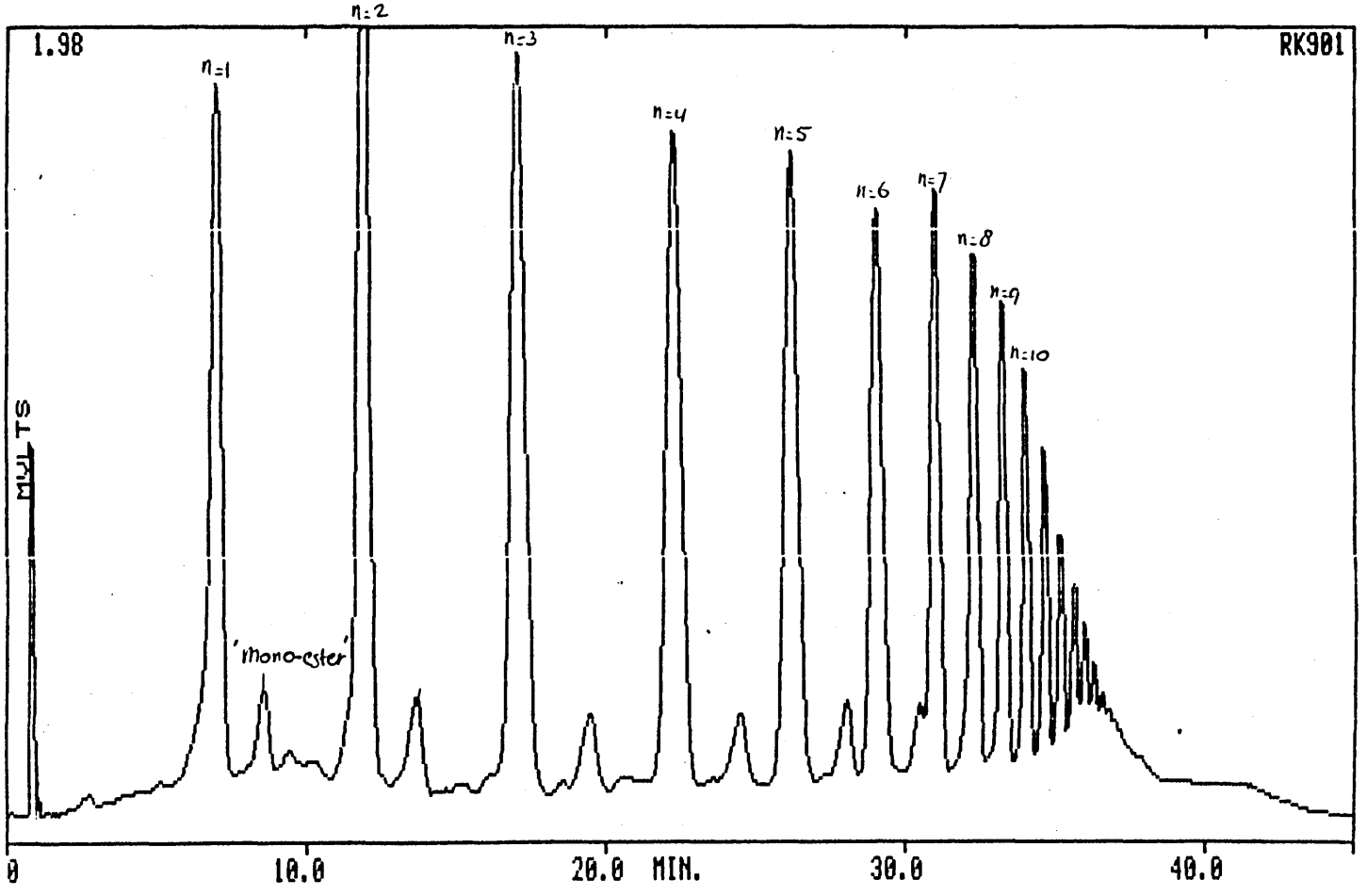


Figure 3.7 HPLC Trace For Low Molar Mass PBT (RK901)

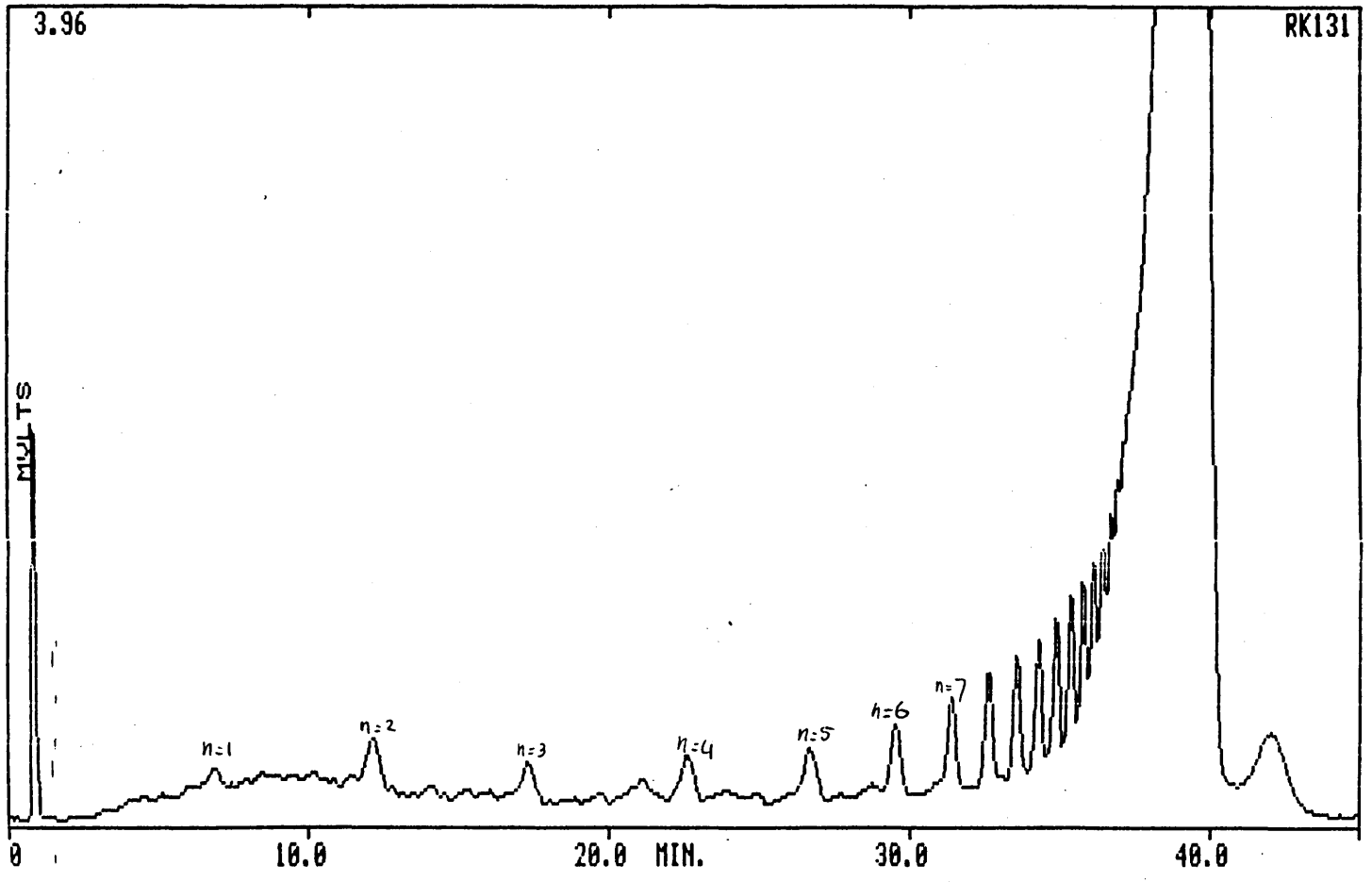
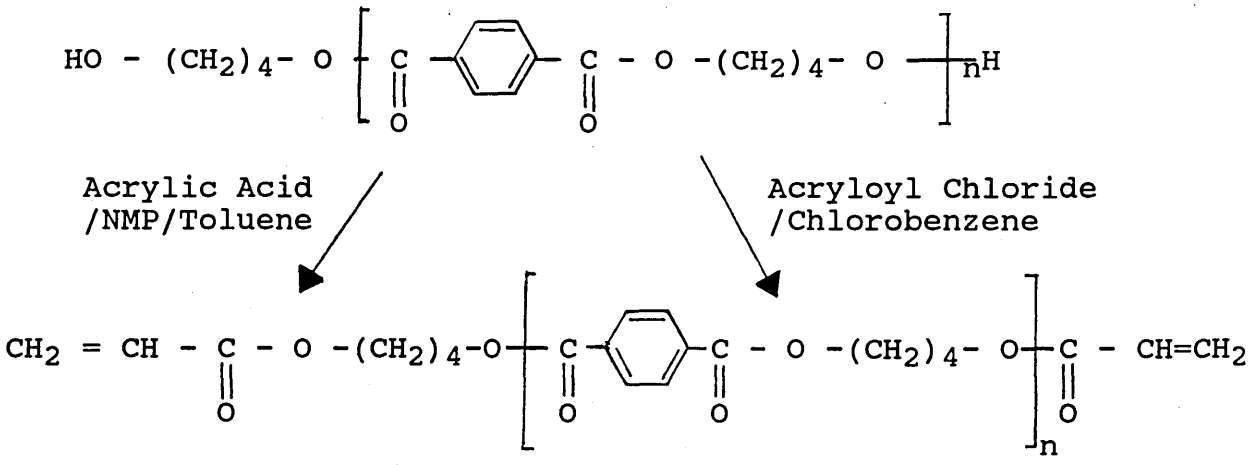


Figure 3.8 HPLC Trace For PBT Oligomer (RK131)

(RMM = 6097)

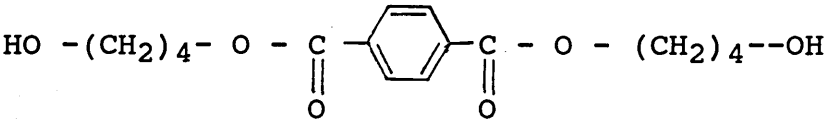
polycondensation step (i.e. RK 123, 131, 143), the number of low molar mass oligomeric species present is significantly reduced, since they have been involved in both stages of polyester formation. (Fig. 3.8).

3.322 Vinyl Functionalised PBT by Solution Methods



Reaction Scheme 3.10 Preparation of Vinyl Terminated PBT Oligomers by Solution Technique

The initial investigation into solution functionalisation of PBT, was performed using PBT monomer for model reactions



The monomer was synthesised from dimethylterephthalate and butane diol in excess, with tetraisopropyl orthotitanate as catalyst. Unreacted butane diol was removed by pouring the reaction product in excess water, after which a filtration step was carried out. The monomer product obtained was then recrystallised from a benzene solution.

In initial functionalisations of the monomer with acryloyl

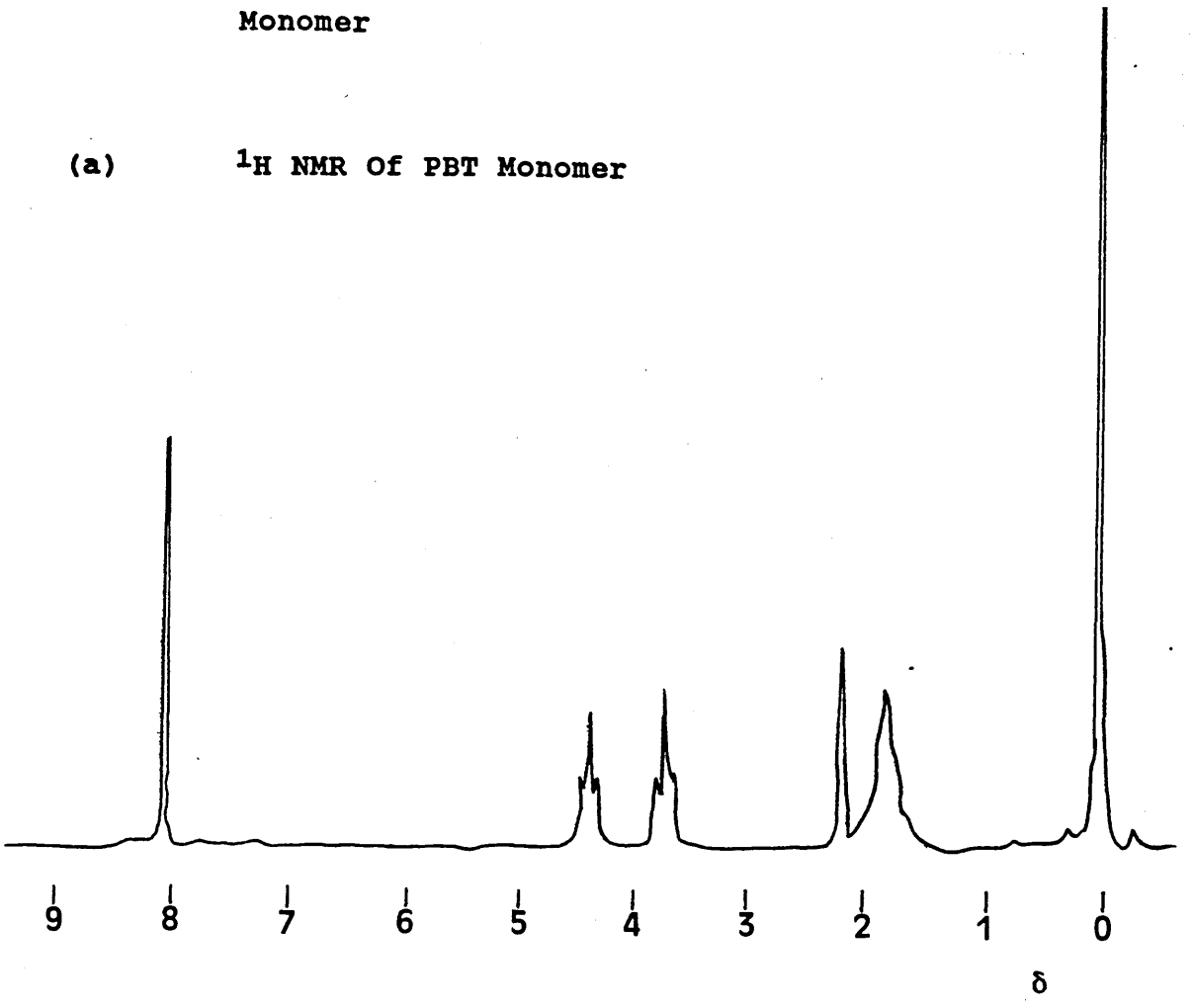
chloride, pyridine was employed as the base in the reaction with dichloromethane as solvent. However, problems were encountered with emulsion formation during the removal of excess base with acid washes. Carlini et al (189,190), have carried out a successful reactions between acryloyl chloride and hydroxy terminated compounds. In each case triethylamine was used as the base.

The use of triethylamine appeared to alleviate the problem of emulsion formation somewhat, but not completely. Emulsion formation was eventually overcome by removing solvent and excess volatiles by rotary evaporation of the reaction mixture. Spectroscopic analysis (Fig. 3.9) indicated a successful reaction, with fewer impurities in the final product when THF rather than dichloromethane was used as solvent.

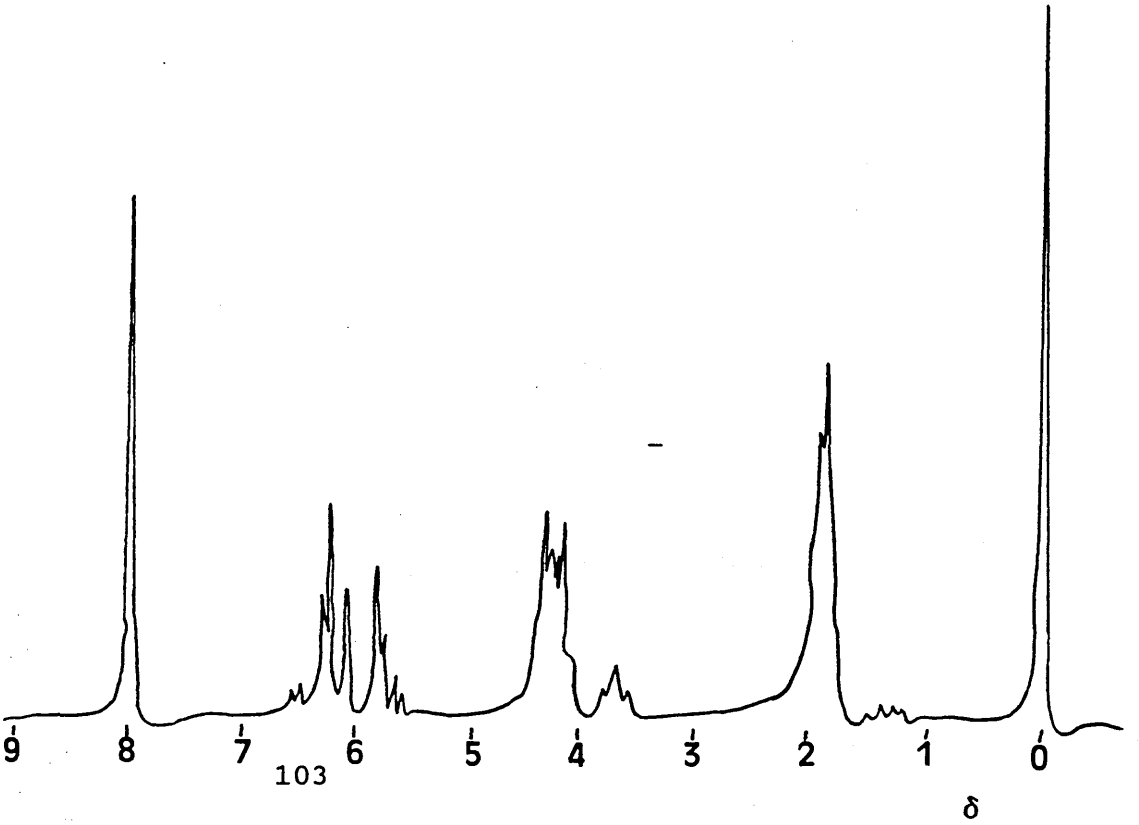
Acrylic acid was also used to functionalise the monomer and proved to be successful. However, a gel-like material occurred in the reaction mixture. A possible cause of this could be attributed to the thermal polymerisation of acrylic acids since the gel was more noticeable in reactions carried out in higher boiling point solvents.

Monomer

(a) ^1H NMR Of PBT Monomer



(b) ^1H NMR Of PBT Monomer + Acryloyl Chloride



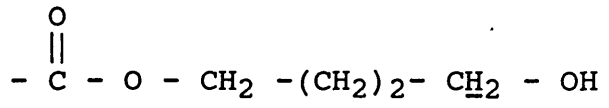
The esterification reaction that is used for vinyl functionalisation of the monomer is not as applicable to the higher oligomers, because acrylic acid could react with the typical solvents for PBT (191). The same problem occurs for the acid chloride.

N - methyl pyrrolidone has been shown to be a good solvent for PBT above 150°C (192), and would theoretically not interfere with the esterification. Other possible solvents for copolymerisation included chlorobenzene, commonly used for the synthesis of a wide range of PDMS block copolymers (75,109,121,136,193). This along with 1, 2 dichlorobenzene was investigated as a solvent for low molar mass PBT oligomers. PBT proved to be soluble in both solvents at their respective reflux temperatures (chlorobenzene 132°C, dichlorobenzene 178°C). Owing to its lower boiling point chlorobenzene was chosen as solvent for the acryloyl chloride reaction. A NMP/toluene (67/33) solvent mixture was chosen for the esterification, since the water by-product formed during the reaction could be removed by azeotropic distillation

For each of the reactions shown in Reaction Scheme 3.10 a twenty fold excess of the vinyl group containing precursor was used as well as long reaction times. These forcing conditions were used to see if functionalisation was possible using solution techniques.

The use of acryloyl chloride proved to be the most successful solution technique. The infra-red spectrum showed a reduction in the intensity of the O - H stretching frequency at 3410 cm^{-1}, together with the appearance of a small peak at 1630 cm^{-1} indicative of C = C stretching bands. A small peak at 980 cm^{-1} corresponding to an alkene C - H stretching vibration is present but this is usually associated with a second peak at 940 cm^{-1}. Unfortunately the peak in this region is masked by signals associated with PBT.

The ^{1}H NMR shows a multiplet signal of 6 - 6.5 δ which indicates the presence of vinyl protons. There is however, still a signal at 4.0δ where the resonance due to methylene protons adjacent to hydroxyl groups would be expected to appear.



The signal is reduced in intensity and the triplet signal at 4.5 δ assigned to the methylene protons adjacent to the carbonyl group has become more prominent. It appears that some functionalisation has occurred.

During the reaction some material became solubilised in the chlorobenzene and the ^{1}H NMR of this product proved to be very similar to the product found to be insoluble in chlorobenzene. A possible explanation for this is that lower molar mass oligomers of PBT present in such samples

are more soluble in chlorobenzene and they remain in solution when the solution is cooled.

The I.R. and ^{1}H NMR spectra obtained of the reaction products when attempting the functionalisation using acrylic acid were very similar to those of the oligomeric starting materials. No signals corresponding to the vinyl protons were found to be present, indicating that functionalisation possibly was unsuccessful. During the reaction the solution became discoloured and eventually turned black, which is probably due to the decomposition of n - methyl pyrrolidone (194).

Discolouration of the reaction mixture also occurred when 10-undecenoyl chloride was used to functionalise PBT oligomers with NMP as solvent. The reaction product proved to be PBT with little reaction apparently occurring.

3.323 Vinyl Functionalisation of PBT Oligomers Using Melt Methods

Functionalisations via melt techniques were carried out using a similar method to that used by Sorenson and Campbell (195). 10 - undecenoic acid and 10 - undecenoyl chloride were used for this purpose, since at melt temperatures of PBT, 230^{o}C, acrylic acid and acryloyl chloride would be too volatile. Triethylene glycol phosphoric acid (TEGPA) was added to deactivate the transesterification catalyst (tetrabutyl titanate) used in the preparation of α, ω hydroxy PBT (168). Deactivation

occurs by complexation between TEGPA and the titanate. Shortly after the undecenoic acid had been added to the reaction, small droplets of moisture began to gather around the top of the vessel. This is expected since water is liberated when reaction occurs.

Samples were removed after fifteen minutes and seventy five minutes. The disappearance of the hydroxyl peak (3410 cm^{-1}) was observed after fifteen minutes along with the emergence of peaks at 1640 cm^{-1} (C = C stretch) and 990 cm^{-1} ($RCH = CH_2$). In the I.R. of the final product the signals due to hydroxyl groups had disappeared and the peaks associated with the vinyl groups were present,(see Figs. 3.10, 3.11).

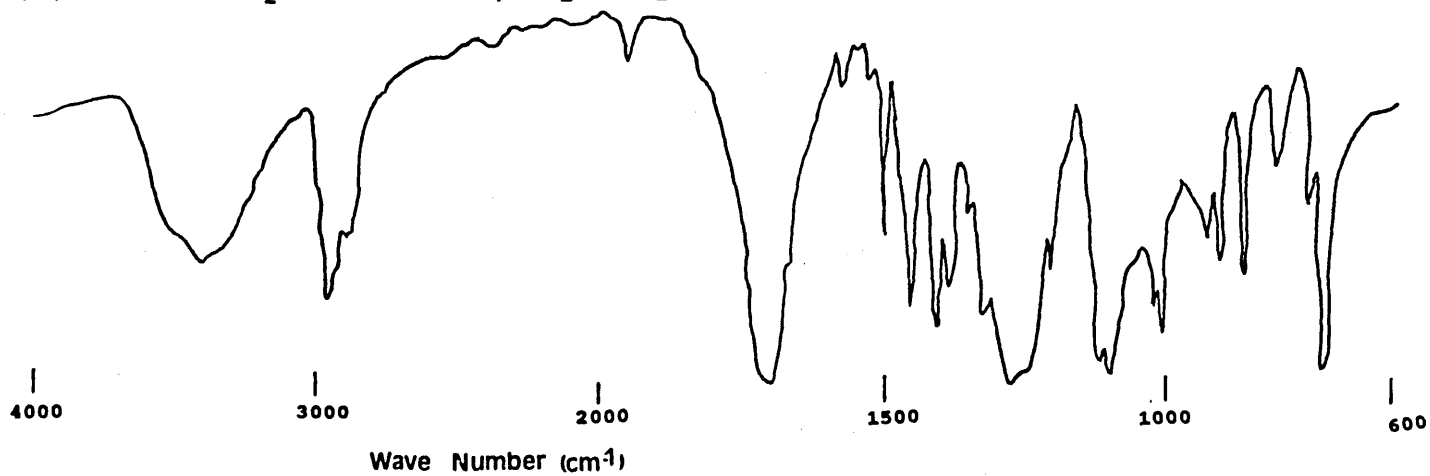
The ^{1}H NMR (Figs. 3.12) gives further evidence that the reaction had been successful as follows:

(i) The methylene proton at 3.9δ is no longer apparent.

(ii) The multiplet signal between 5 - 6δ is characteristic of vinyl protons.

(iii) The presence of signals between 1 - 2.5δ are characteristic of undecenoic acid.

(a) I.R. Spectrum Of α, ω Hydroxy PBT



(b) I.R. Spectrum Of PBT + Undecenoic Acid

After 10 Minutes

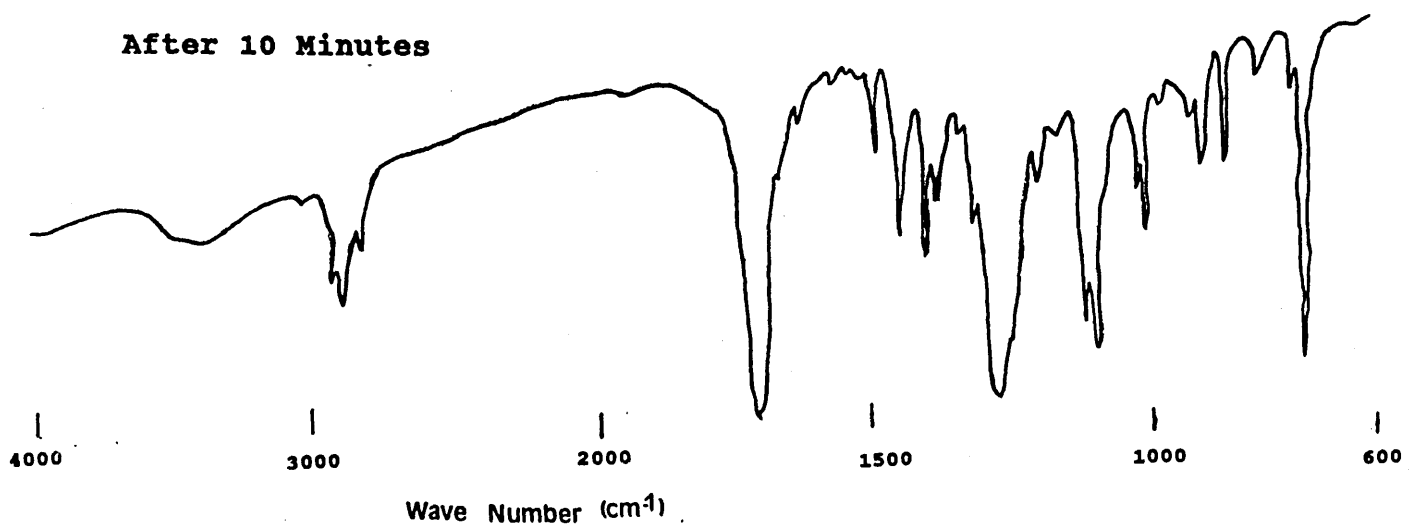
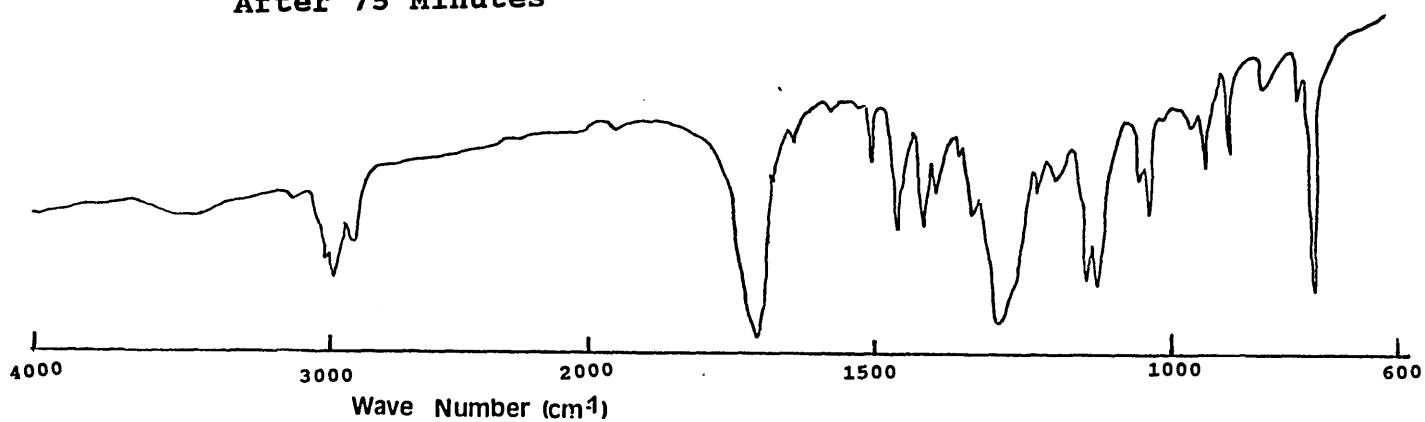


Figure 3.10 I.R. Analysis Of Vinyl Functionalised Oligomeric PBT

(a) I.R. Spectrum Of PBT + Undecenoic Acid

After 75 Minutes



(b) I.R. Spectrum Of Reaction Product Of PBT

With Undecenoic Acid

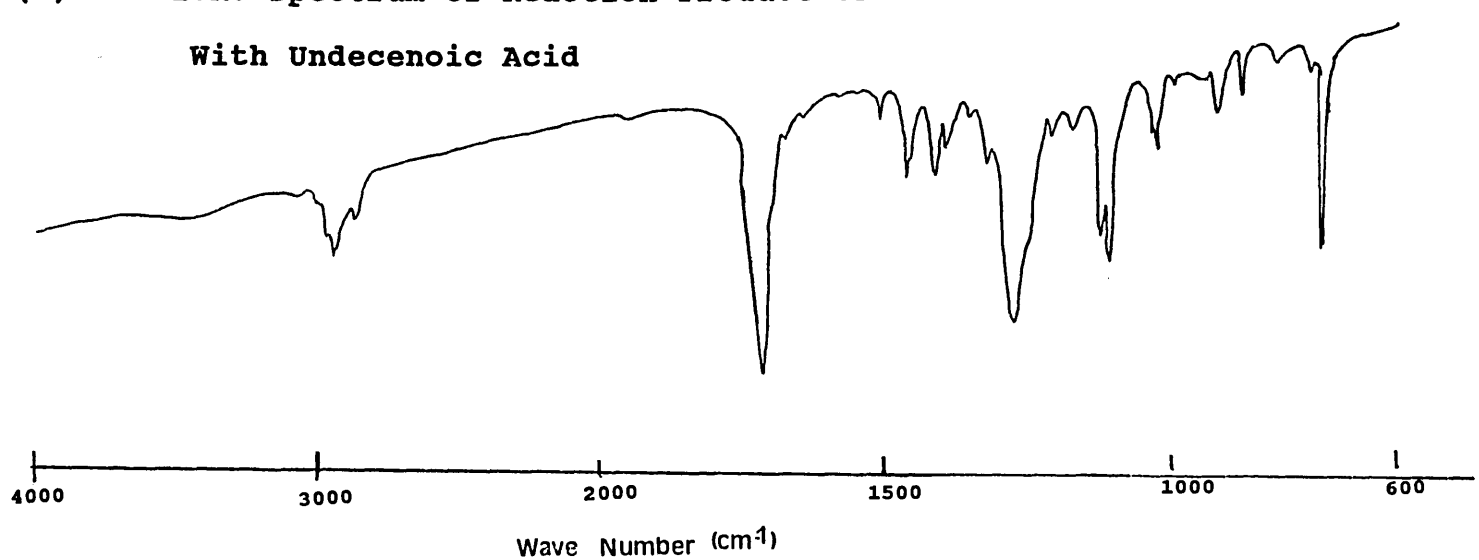
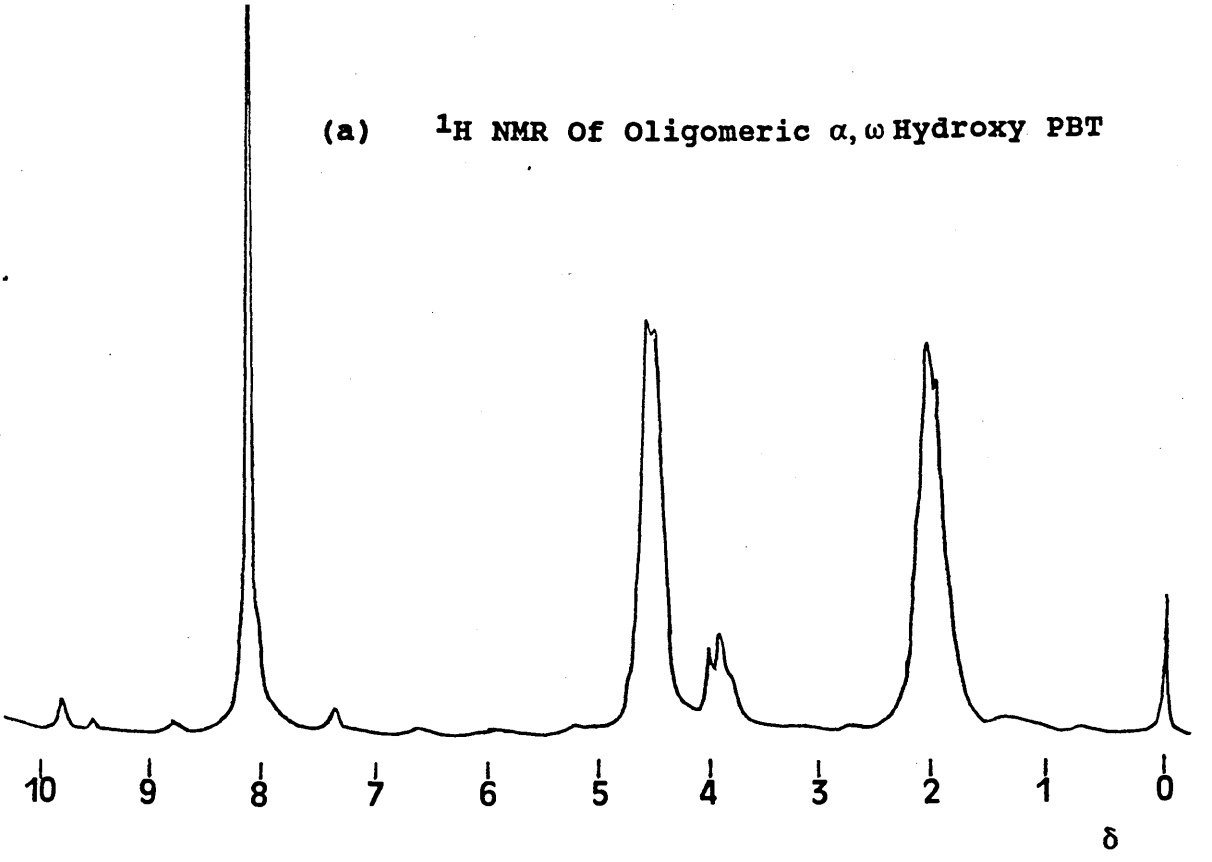
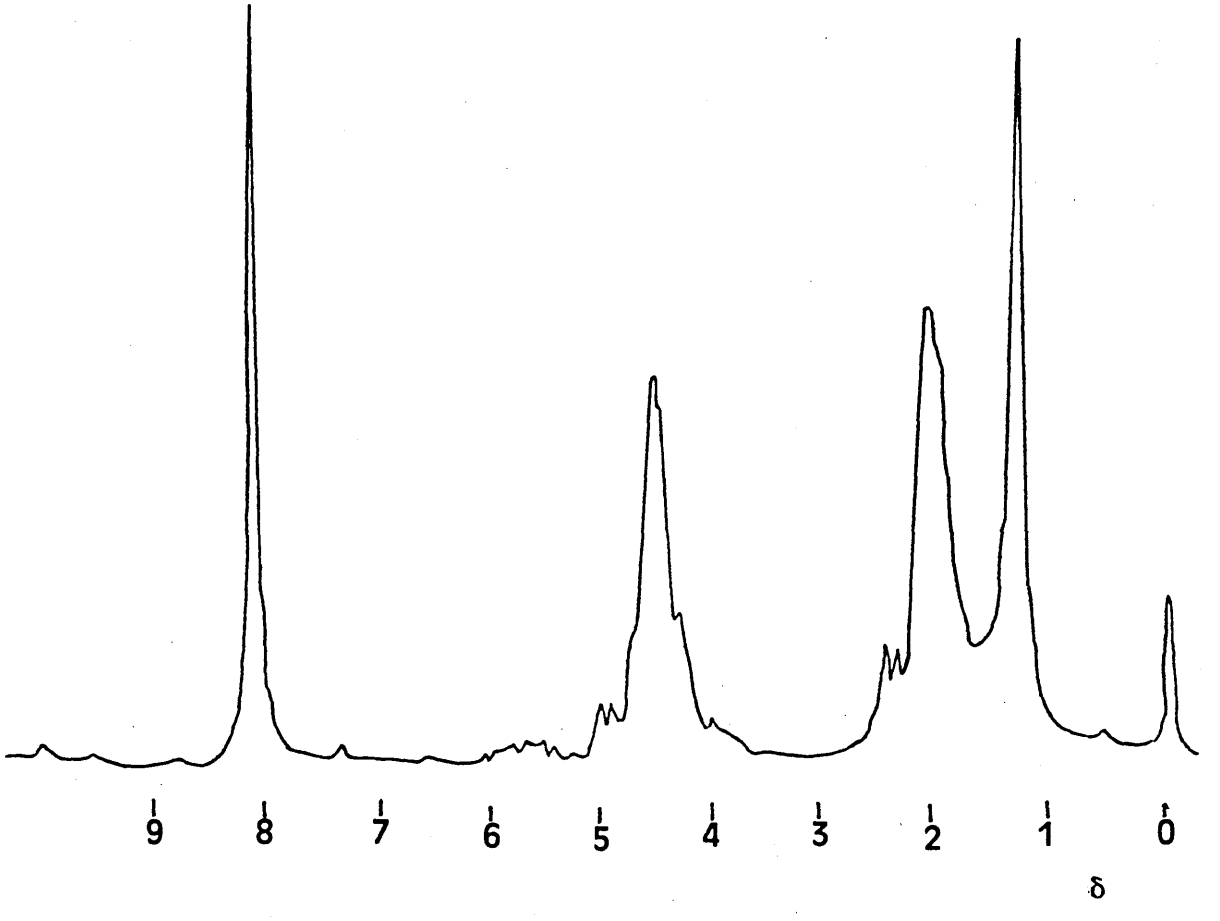


Figure 3.11 I.R. Analysis Of Vinyl Functionalised Oligomeric PBT

(a) ^1H NMR Of Oligomeric α, ω Hydroxy PBT



(b) ^1H NMR Of Reaction Product Of PBT With Undecenoic Acid

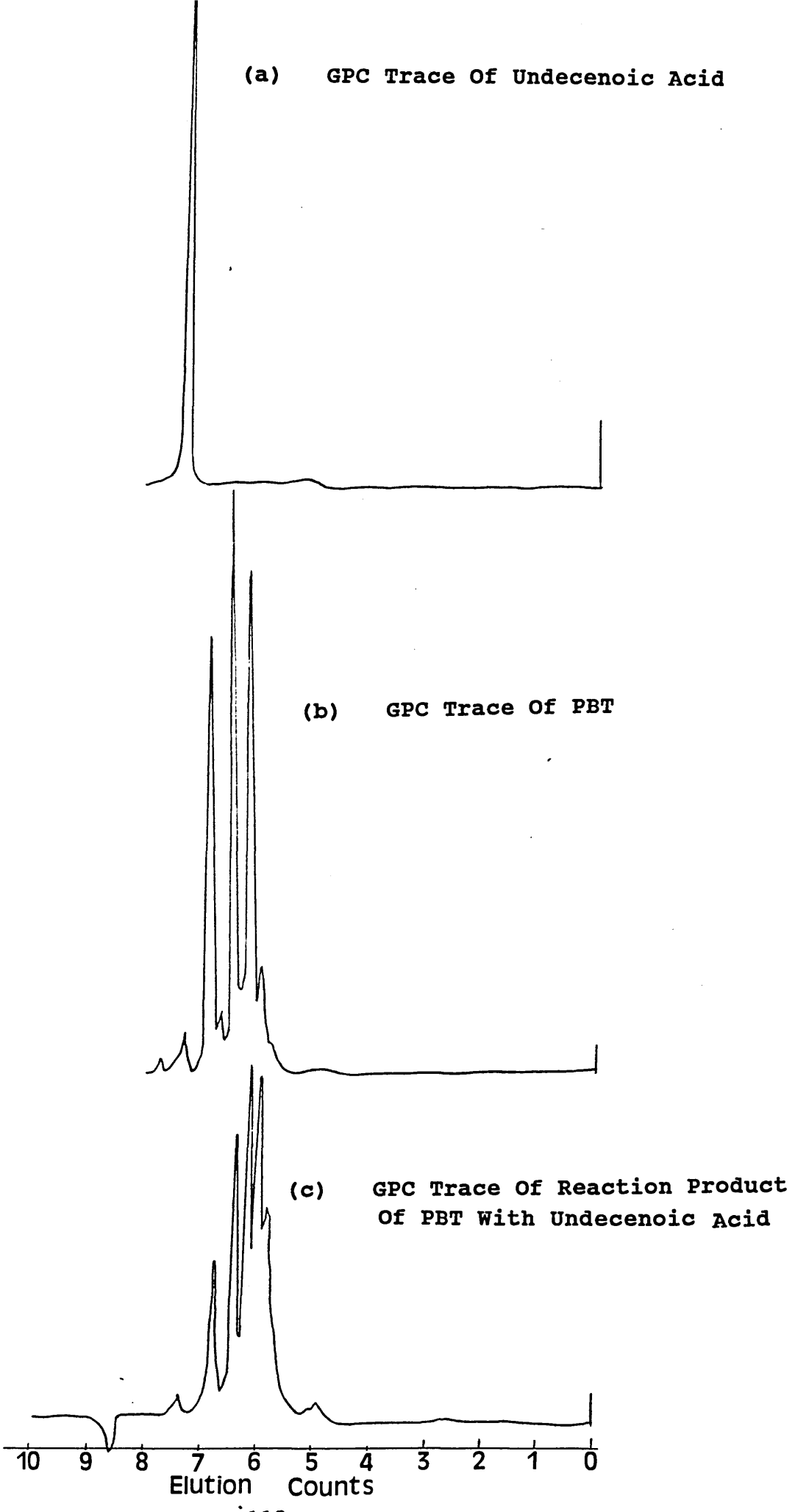


Although the I.R. spectrum of the product indicates that there is no free undecenoic acid present in the product (no broad O - H str peak 3000 - 2600 cm^{-1}), further confirmation was provided by GPC analysis, (Fig. 3.13). Some of the lower oligomers of the functionalised PBT were extracted into THF and then analysed. Unfortunately at the position where free undecenoic acid elutes so does an oligomer of PBT. However, there is no significant increase in the intensity of the functionalised PBT peak as compared to that of the α, ω hydroxy PBT peak. Therefore, it is unlikely to be free undecenoic acid that is responsible for a signal in the region where signals for vinyl groups are to be expected.

When undecenoic acid is initially added to the mixture two phases are normally visible with a white colouration at the interface. This is probably due to localised cooling of the PBT. A homogenous mixture is formed on faster stirring.

The functionalisation was performed with undecenoyl chloride and numerous times utilising undecenoic acid. A variety of different catalytic species were employed with undecenoic acid in an attempt to optimise the conversion of hydroxyl groups.

In the first series of experiments using undecenoic acid, initially no specific catalyst was used and any tetrabutyl tit anate had been deactivated with TEGPA.


(a) GPC Trace Of Undecenoic Acid
(b) GPC Trace Of PBT
(c) GPC Trace Of Reaction Product Of PBT With Undecenoic Acid
10 9 8 7 6 5 4 3 2 1 0
Elution Counts

Secondly a classical esterification catalyst, p-toluene sulphonic acid was tried. Finally in this series 10-undecenoyl chloride was investigated with no specific catalyst and short reaction times (~30 min). In this trial, on addition of the acid chloride, a very vigorous reaction took place with white fumes of hydrogen chloride liberated. Successful functionalisation occurred in all cases (I.R. and 60MHz ^1H NMR) and this was further supported by DSC analysis (Table 3.7) which showed a decrease in the melting endotherm of PBT in each case.

TABLE 3.7 DSC Analysis of Melt Functionalised PBT Oligomers

Sample	Melting Pt. /^oC	$\triangle H$ J/G
PBT (RK 901)	215.9	56.71
PBT + Undecenoic Acid	187.5	31.60
PBT + Undecenoic Acid + p- TSO_3H	188.9	35.01
PBT + Undecenoyl Chloride	188.6	30.60
PBT Blank	210.7	54.71

The drop in melting temperature and enthalpy of melting are due to the attachment of the long alkyl chain which disrupts the crystallinity of the PBT.

Further ^1H NMR analysis (270 MHz) (Fig 3.14) showed that greater than 90% conversion of the undecenoic acid had been obtained in each case. It also indicated that the p - toluene sulphonic acid catalysed functionalisation showed

the greatest conversion of hydroxyl groups (Table 3.8). However, the terminal vinyl groups appear to undergo a side reaction in this case, which is probably an isomerisation where the terminal unsaturation becomes internal.

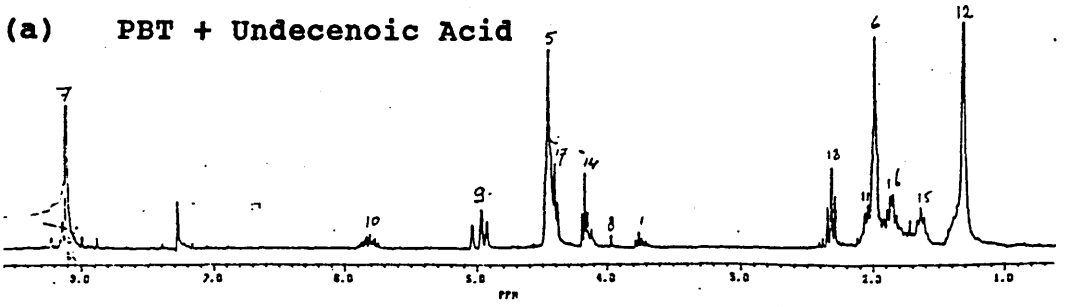
$$- CH_2 - CH = CH_2 \longrightarrow - CH = CH - CH_3$$

Table 3.8 Degree of Functionalisation of PBT Oligomers

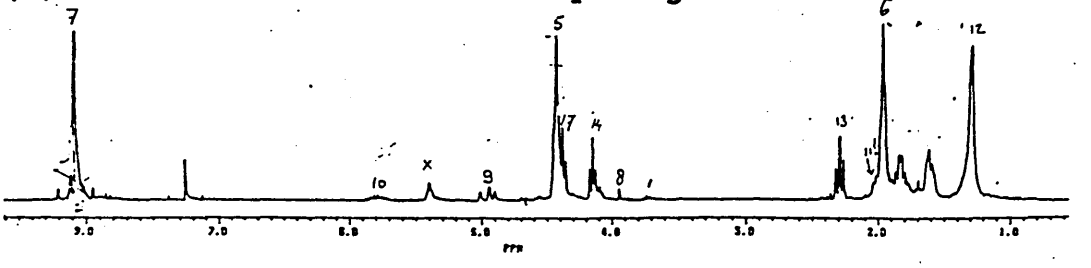
Sample	% OH reacted (14/14 + 1)	% Undecenoic Acid Reacted (14/13)	Relative Molar Mass
PBT+Undecenoic Acid	78	91	900
PBT+Undecenoic Acid+ p-TSO3H	89	95	1000
PBT+Undecenoyl Chloride	79	95	900
PBT Blank	-	-	1300

The highest conversion was further confirmed by HPLC, with no traces of unreacted oligomers present in the sulphonic acid catalysed functionalisation. However in the other two cases, traces of unreacted oligomers can be seen (Fig. 3.15).

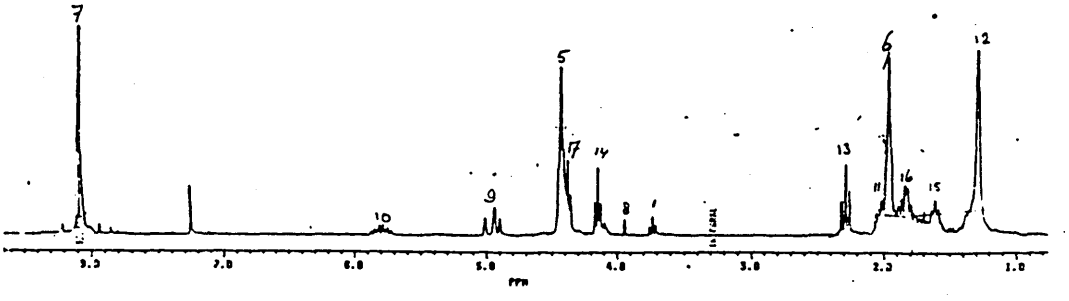
(a) PBT + Undecenoic Acid



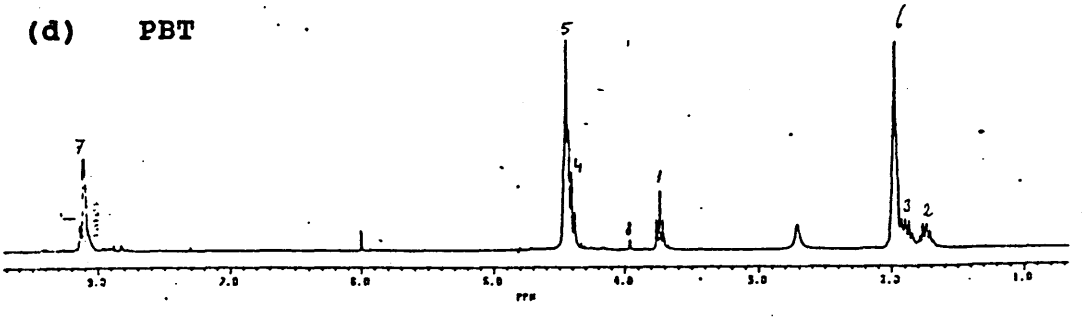
(b) PBT + Undecenoic Acid + p-TSO_3H

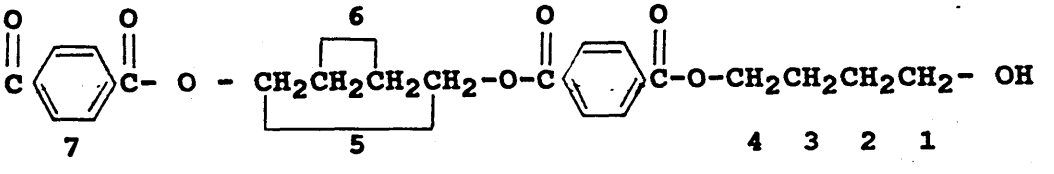


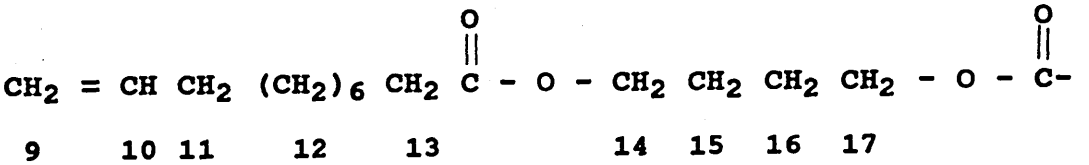
(c) PBT + Undecenoyl Chloride

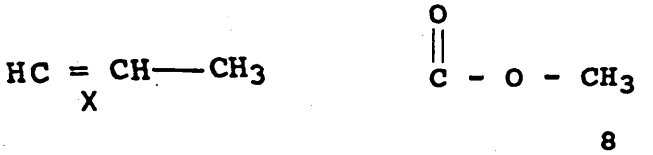


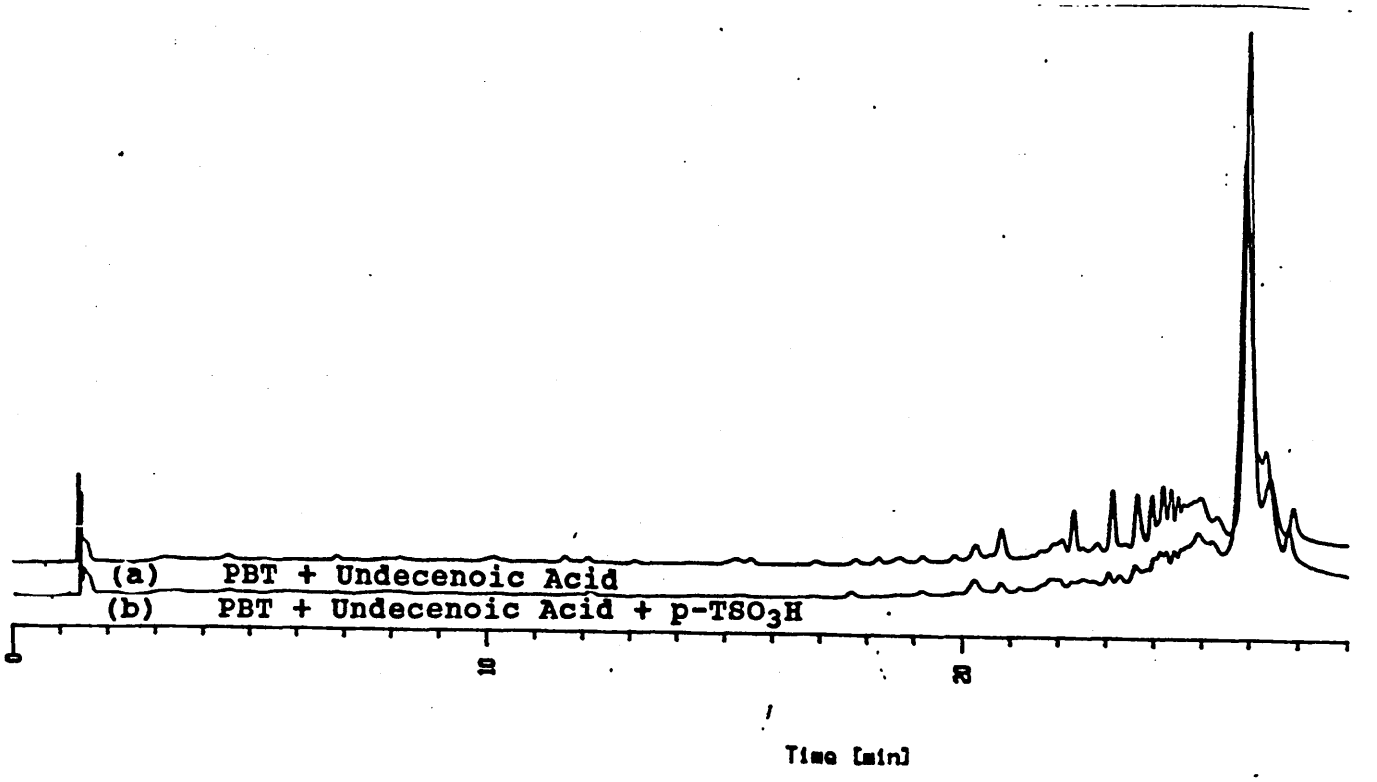
(d) PBT

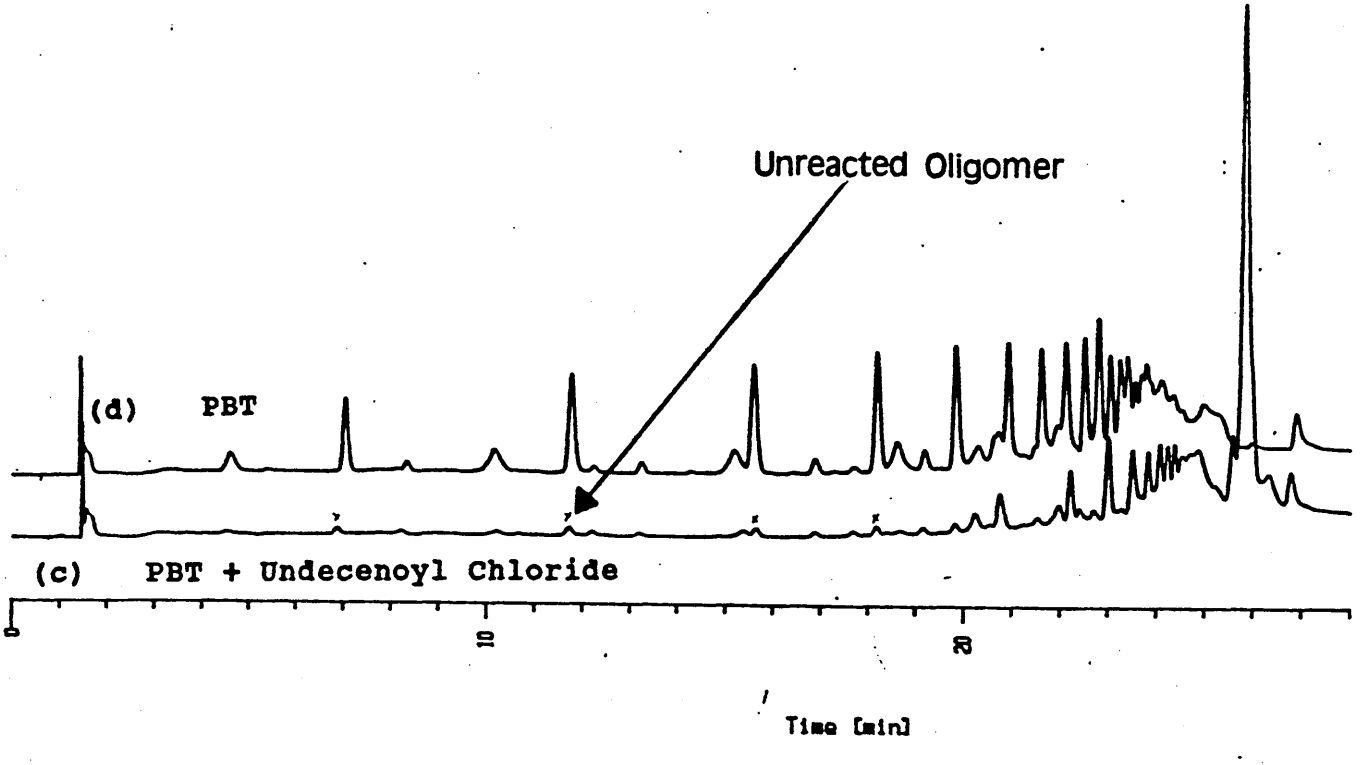









(a) PBT + Undecenoic Acid
(b) PBT + Undecenoic Acid + p-TSO3H
Time [min]


Unreacted Oligomer
(d) PBT
(c) PBT + Undecenoyl Chloride
Time [min]

In a second series of functionalisations with undecenoic acid, the catalytic species stannous octoate and the titanate already present in some samples of PBT were investigated. However, in this series of experiments, a vacuum programme of 5.0 mmHg for forty five minutes, was used. This was done in an attempt to improve the conversion of the hydroxyl groups, without using p - toluene sulphonic acid. Initial spectroscopic evidence (I.R. and 60 MHz ^{1}H NMR) showed the functionalisation to be successful. ^{1}H NMR (270 MHz) analysis showed no free hydroxyl groups to be detectable and the percentage conversion of undecenoic acid to be improved (Table 3.9).

Table 3.9 Degree of Functionaliisation of PBT Oligomers Utilising a Vacuum Programme

Sample	% Undecenoic Acid Reacted	Relative Molar Mass
1	97	2800
2	99	2800
3	94	2300
4	-	5200

Sample Index (Tables 3.9 & 3.10)

1. PBT(RK 101) + Undecenoic Acid + Vacuum Programme (Temp 245^{o}C)

2. PBT(RK 101) + Undecenoic Acid + TEGPA + Vacuum Programme (Temp 245^{o}C)

3. PBT(RK 101) + Undecenoic Acid + TEGPA + Stannous Octoate (~2000 ppm) + Vacuum Programme (Temp 245^{o}C)

4. PBT(RK 101) + TEGPA + Vacuum Programme (Temp 245^{o}C)

However, although a greater conversion is obtained in the second series of functionalisation experiments there is a concurrent increase in relative molar masses of the samples. The possible explanation for this observation is that in this series of functionalisations a reaction temperature of 245°C and a vacuum programme of forty five minutes were used. This is compared previously with a reaction temperature of 230°C and no vacuum programme. The former conditions are likely to promote polycondensation and/or evaporation of oligomers resulting in the observed increase in relative molar mass.

Further evidence of the increased relative molar mass was observed in that the samples were too high for HPLC and an increase was seen in the melting endotherm of each sample as compared with the first series of experiments (Table 3.10).

Table 3.10 DSC Analysis of Melt Functionalised PBT Oligomers Utilising a Vacuum Programme

Sample	$\triangle$H J/g	Peak Temp °C
1	53.57	210.6
2	51.40	210.5
3	53.54	210.9
4	57.21	220.1
RK 101	61.66	222.4

The results of the melt polymerisation were much more satisfactory than any of those obtained by solution and all further functionalisations for block copolymerisation experiments were carried out by melt methods, using undecenoic acid in preference to the very reactive undecenoyl chloride. The route chosen to functionalise the PBT oligomers was to use no specific catalyst but to deactivate the titanate with TEGPA and utilise a very short vacuum programme (~ 10 min) to limit molar mass increases.

4. SYNTHESIS AND CHARACTERISATION OF PBT - PDMS BLOCK COPOLYMERS

4.1 Introduction

Melt and solution techniques have been investigated for synthesis of block copolymers of PBT and PDMS. A major problem associated in synthesising copolymers of this type is the incompatibility of the two block components. The Hildebrand solubility parameters of PBT and PDMS are 21.5 $(MJm^{-3})^{1/2}$ and 14.9 $(MJm^{-3})^{1/2}$ respectively. For complete compatibility the difference in the solubility parameters is usually less than $0.4(MJm^{-3})^{1/2}$. Incompatibility is observed with differences of $0.8(MJm^{-3})^{1/2}$ and greater. The two polymers under investigation are very incompatible, which is reflected by their own common solvents, eg. toluene for PDMS and hexafluoroisopropanol for PBT. Solvents which disolve both PDMS and PBT are limited in number. A variety of solvents has been investigated during this work for the preparation of homogeneous solutions of PDMS and PBT.

Melt techniques have been employed for copolymer synthesis since the number of acceptable solvents are very few. This approach involves the addition of a suitably functionalised PDMS oligomer to a molten mutually reactive PBT oligomer.

A number of organic reactions such as hydrosilation, transesterification, transamidation, epoxy - hydroxyl, esterification, and isocyanate - hydroxyl have been considered as routes to link the two polymers. The objective of each of these routes was to have Si - C links in the copolymers rather than the hydrolytically unstable Si - O - C links (100,122).

4.2 Experimental

4.21 Characterisation Methods

4.211 General Directions

Infrared spectra were recorded on a Perkin-Elmer 783 infrared spectrophotomer and were determined using potassium bromide (KBr) discs or as cast films from chloroform solution, unless otherwise stated.

Nuclear magnetic resonance (NMR) spectra were obtained using either a Jeol 60 MHz spectrometer, a Bruker WP-80 (80MHz) spectrometer or a Bruker AM-270 (270MHz) spectrometer. For copolymer samples the solvent used was deuterochloroform or deuterated tetrachloroethane. Tetramethylsilane (TMS) was used as an external standard, and the chemical shifts are reported on the δ scale.

Differential scanning calorimetry (DSC) was used to characterise thermal transitions of the block copolymers. All measurements were performed using a Mettler DSC 30, (a computer controlled instrument with a dedicated Mettler TC10 TA processor). The cell was heated at a rate of 10K

min^{-1}. All test samples weighed about 10 to 20 mg.

4.212 Dynamic Mechanical Analysis.

The dynamic mechanical behaviour of the copolymers was investigated. For this type of analysis the relationship between the dynamic properties and structural parameters (crystallinity, molecular orientation, relative molecular mass, crosslinking, copolymerisation etc) and external variables (temperature, time, frequency etc) can be studied. In order to determine the dynamic mechanical properties (such as dynamic modulus E', the loss modulus E'' and the damping or internal friction $\tan \delta = (E''/E')$, various vibrational methods are used. Dynamical tests measure the response (deformation) of the material to a sinusoidal or other periodic stress. The type of instruments include free vibration, resonance forced vibration and wave or pulse propagation devices. Most measure either shear or tensile properties and instruments are available to measure bulk properties. Dynamic tests over a wide temperature and frequency range are especially sensitive to the chemical and physical structure of plastics. Such tests are in many cases the most sensitive tests known for studying glass transitions and secondary transitions in polymers, as well as the morphology of block copolymers.

Elastic materials convert mechanical work into potential energy which is recoverable for example, in an ideal spring (Hooke's law), no energy is converted into heat. However, Newtonian liquids flow if subjected to a stress and the energy is not stored, but almost entirely dissipated as heat and flow, thus they possess a high degree of damping.

Viscoelastic polymers display the characteristics of both an elastic body and a viscous liquid. Hence, if a sinusoidal stress is applied to a viscoelastic material, the resulting strain will also be sinusoidal of the same frequency, but will lag behind the applied stress by phase angle δ. The magnitude of δ depends on the amount of damping in the material. The resulting strain can be described in terms of its angular frequency, ω, and the maximum amplitude ε_o.

$$\varepsilon = \varepsilon_o \exp i\,\omega t \quad \text{(Eqn 4.1)}$$

The relation between stress and strain

$$\sigma = \varepsilon E^*$$

$$E^* = E' + i\,E'' \quad \text{(Eqn 4.2)}$$

E^* is the frequency dependant complex dynamic modulus, E' is the storage modulus and E'' is the loss modulus, and the phase angle δ is given by

$$\tan \delta = E''/E' \quad \text{(Eqn 4.3)}$$

Equation (4.3) is thus, a measure of the ratio of energy lost to that stored in the material during one cycle of oscillation.

All measurements reported here, were carried out with a Dynamic Mechanical Thermal Analyser (DMTA) manufactured by Polymer Laboratories Ltd. The samples used for the DMTA were homogenous and the thickness of the samples were obtained by averaging many thickness gauge readings.

All samples were tested at a frequency of 10Hz. A strain amplitude of x1, corresponding to a 0.016 mm displacement was used in all experiments. Plots of tan δ dynamic storage modulus, E' and dynamic loss modulus, E'' were provided by the dedicated computer system.

4.22 Solution Techniques

4.221 Synthesis of PBT - PDMS Block Copolymers by Hydrosilation in Chlorobenzene

α, ω - Bis(10 - undecenyl) PBT (di vinyl PBT) (5g, 5.55×10^{-3} moles) together with dry chlorobenzene (50 mls) was placed in a three-necked light sealed flask equipped with dropping funnel, condenser and nitrogen inlet. A solution of α, ω di (hydrosilane) PDMS (3.38g, 5.55×10^{-3} moles) in chlorobenzene (15 mls) was placed in the dropping funnel, freshly prepared hexachloroplatinic acid (1.11×10^{-6} moles) solution in dry THF was added to the flask.

The silane solution was added slowly to the refluxing solution of divinyl PBT. The silane was added slowly over a one hour period and then the reaction mixture was refluxed for forty eight hours.

During reflux a homogenous mixture developed, but on cooling a viscous milky white liquid was obtained. Excess solvent was removed by evaporation and the reaction product dried further in the vacuum oven at 110°C and 10 mmHg. A white waxy solid was obtained.

A sample of the reaction product was placed in a soxhlet finger and continually extracted into toluene for forty eight hours. The material remaining in the finger was then dried in the vacuum oven. The excess toluene was removed from the extract by rotary evaporation. The extracted material and the material remaining in the soxhlet finger were analysed by I.R., ^{1}H NMR and DSC.

4.222 Synthesis of PBT - PDMS Block Copolymers by Hydrosilation in Tetrachloroethane/Nitrobenzene

A solution of divinyl PBT (5g, 5.55×10^{-3} moles) in tetrachloroethane (99.5)/nitrobenzene (0.5) (50 mls) was placed in a light sealed three-necked round bottomed flask equipped with stirrer, condenser and nitrogen inlet. The solution was warmed to 80°C, to give a clear solution, when α, ω di (hydrosilane) PDMS (3.38g, 5.55×10^{-3} moles) together with hexachloroplatinic acid (1.11×10^{-6} moles) were added and the reaction mixture heated at 80°C for eighteen hours. On cooling the cloudy mixture was precipitated into acidified methanol (400 mls). The precipitated polymer was filtered, dried and subjected to I.R., ^{1}H NMR and DSC analyses.

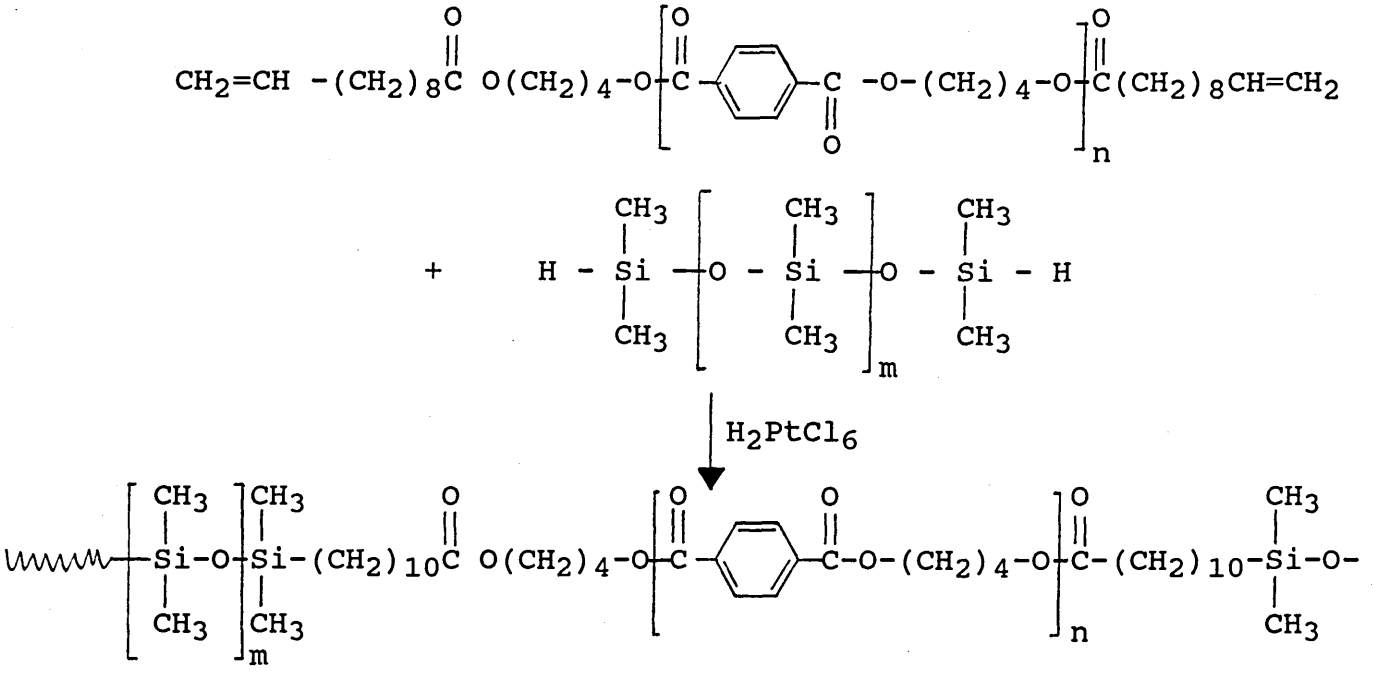
4.23 Melt Techniques

4.231 Reaction of α,ω Hydroxy PBT with α,ω - Bis (10 - carboxydecyl) PDMS

The apparatus used is shown in Fig. 3.2. α, ω hydroxy PBT (10g, 6.23×10^{-3} moles) was placed in the reaction vessel and melted under a nitrogen at mosphere. Triethyleneglycol phosphoric acid (TEGPA) (~ 2,000 ppm with respect to PBT) was then added and the mixture stirred for thirty minutes. Stannous octoate (~ 2500 ppm cf. PBT) was then added and the mixture stirred for a further five minutes. α,ω bis (10 - carboxydecyl) PDMS (14.20g, 6.23×10^{-3} moles) was then added to the reaction vessel and stirred vigorously to ensure complete mixing. After two hours reaction time, a vacuum (~ 6 mmHg max) was applied for forty five minutes. The product was analysed by I.R., ^1H NMR and DSC.

4.232 Reaction of α,ω Bis (10 - undecenyl) PBT with α, ω di(hydrosilane) PDMS

Several trials were carried out using these precursors, details of which are given in Table 4.1. A typical procedure is described below and the melt apparatus shown in Fig. 3.2 was used.



Reaction Scheme 4.1 Reaction of α,ω bis (10 - Undecenyl) PBT with α,ω di(hydrosilane) PDMS

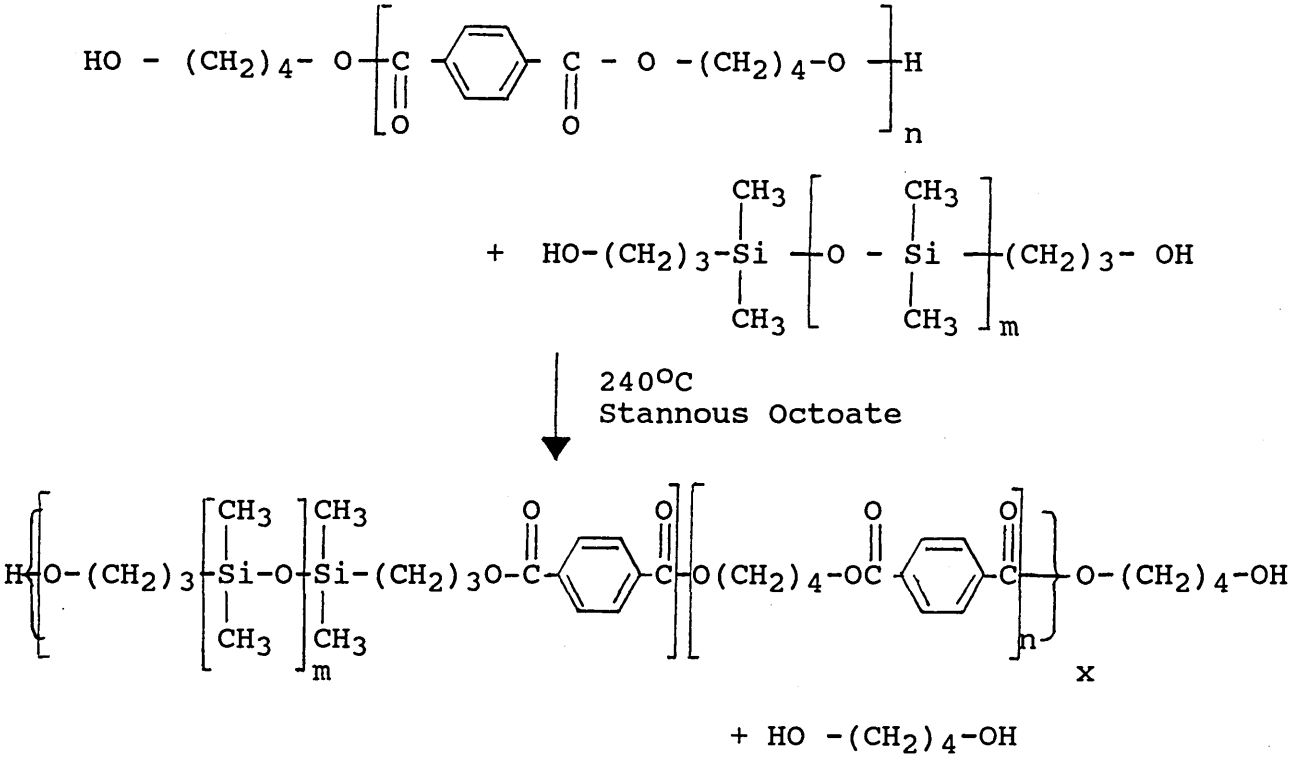
α, ω divinyl PBT (10g, 1.11 x 10^{-2} moles) was dried prior to use in an oven at 130°C. Divinyl PBT was added to the reaction vessel and melted under a nitrogen atmosphere. α, ω di(hydrosilane) PDMS (9.91g, 1.11 x 10^{-2} moles) together with hexachloroplatinic acid (1.176 x 10^{-6} moles in dry THF) was added to the reaction vessel. The reaction was allowed to proceed for approximately two hours with vigorous stirring. All products were analysed by I.R., DSC and where possible by ^{1}H NMR.

TABLE 4.1 Details of Block Copolymer Trials by Hydrosilation

Sample No.	Experimental Details
1	Aged chloroplatinic acid catalyst added with PDMS precursor.
2	80% (by weight) of PDMS precursor added to PBT. After five minutes stirring, remainder of PDMS added together with freshly prepared chloroplatinic acid catalyst.
3	PDMS precursor added to PBT containing chloroplatinic acid catalyst.
4	PDMS precursor, containing chloroplatinic acid catalyst, added in small increments to PBT.
5	PBT and PDMS precursor blended together no catalyst.
6	PDMS precursor and freshly prepared chloroplatinic acid added to PBT. Reaction Time five minutes.
7	As (6) but reaction time fifteen minutes.
8	As (6) but reaction time thirty minutes.
9	As (6) but reaction time sixty minutes.
10	As (6) but reaction time one hundred and twenty minutes.

In sample numbers 1 - 5 the PBT precursor had a RMM of 1600 (RK 101) while in sample numbers 6 - 10 the RMM of the PBT precursor was 2000 (A8 3102).

4.233 Reaction of α,ω Hydroxy PBT with α,ω - Bis Hydroxypropyl PDMS Via Transesterification



Reaction Scheme 4.2 Preparation of PBT - PDMS Copolymers by Transesterification

The melt apparatus as previously shown in Fig. 3.2 was used. Dry α, ω hydroxy PBT (10g, 6.25×10^{-3} moles) was added to the reaction vessel and melted under a nitrogen atmosphere. α,ω hydroxypropyl PDMS (10g, 1×10^{-2} moles) was then added to the reaction vessel. The reaction mixture was stirred vigorously for five minutes before stannous octoate (~ 2,000 ppm) was added. The reaction mixture was stirred rapidly for a further ninety minutes before being subjected to a short vacuum programme (ten minutes 10mm Hg). The product obtained was characterised by I.R., ^{1}H NMR, DSC and DMTA.

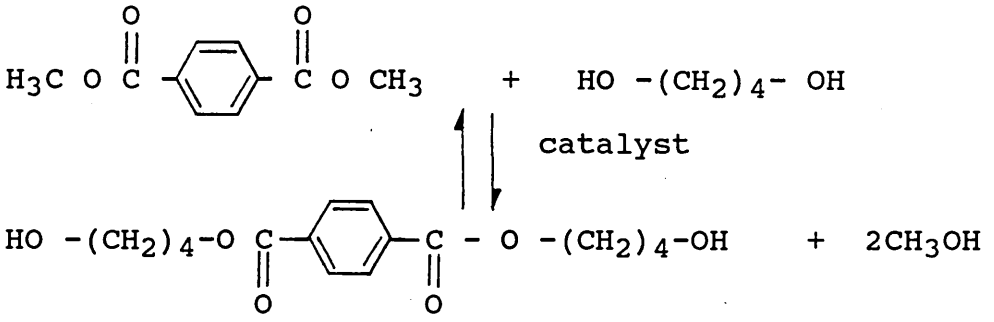
A number of repeat trials were carried out adopting similar procedures. However, a number of parameters were varied, such as catalyst type, condensation period, relative molar masses of the oligomers and reaction times. Details and results of these trials are given in section 4.323.

4.234 Reaction of α, ω, Hydroxy PBT with α, ω - Bis Hydroxypropyl PDMS Via Transesterification Using Mixed Catalyst

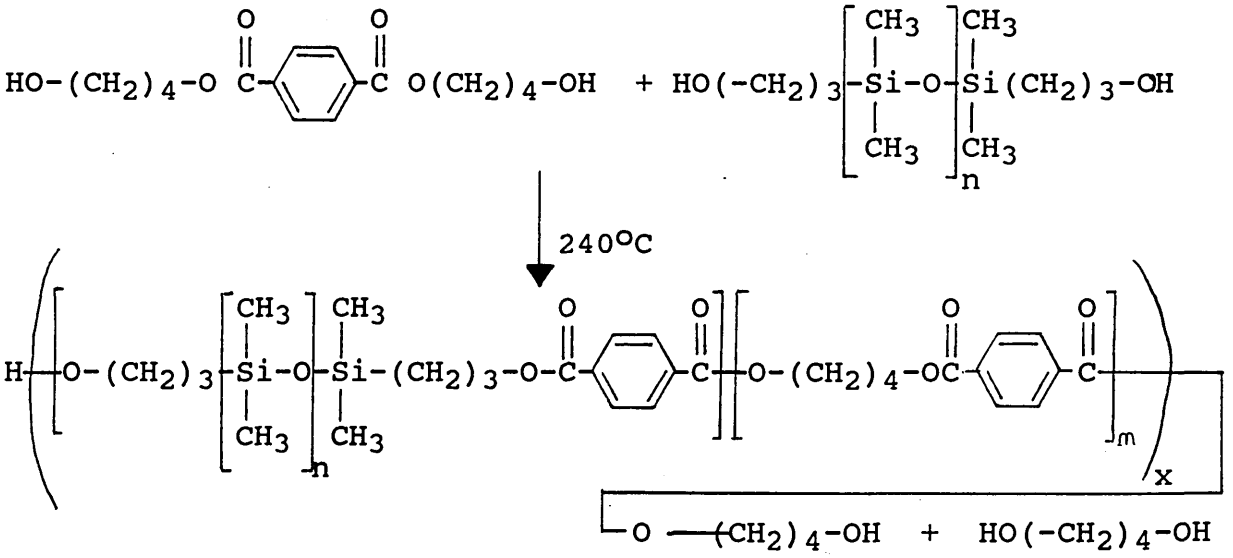
α, ω - hydroxy PBT (10g, 5×10^{-3} moles) was added to the reaction vessel and melted at 240°C in a nitrogen atmosphere. α, ω - hydroxypropyl PDMS (10g, 1×10^{-2}moles) was added to the reaction vessel with stirring. The reaction mixture was then stirred vigorously for approximately five minutes before stannous octoate (~ 2000 ppm) was added. The reaction mixture was then stirred more rapidly (> 120 rpm) for approximately seventy five minutes. Tris-(2,4-di-tert. butylphenyl)-phosphite (Irgafos 168) (~10,000 ppm) was then added and stirring continued for a further thirty minutes. Tetrabutyltitanate (~ 10,000 ppm) was then added and stirring continued for a further fifteen minutes before the pressure was reduced to(<1 mmHg) over about fifteen minutes. A period of approximately sixty minutes was then allowed for polycondensation reactions to take place.

4.235 PBT - PDMS Block Copolymer Synthesis from Monomers of PBT

Step 1 Ester Interchange



Step 2 Polycondensation

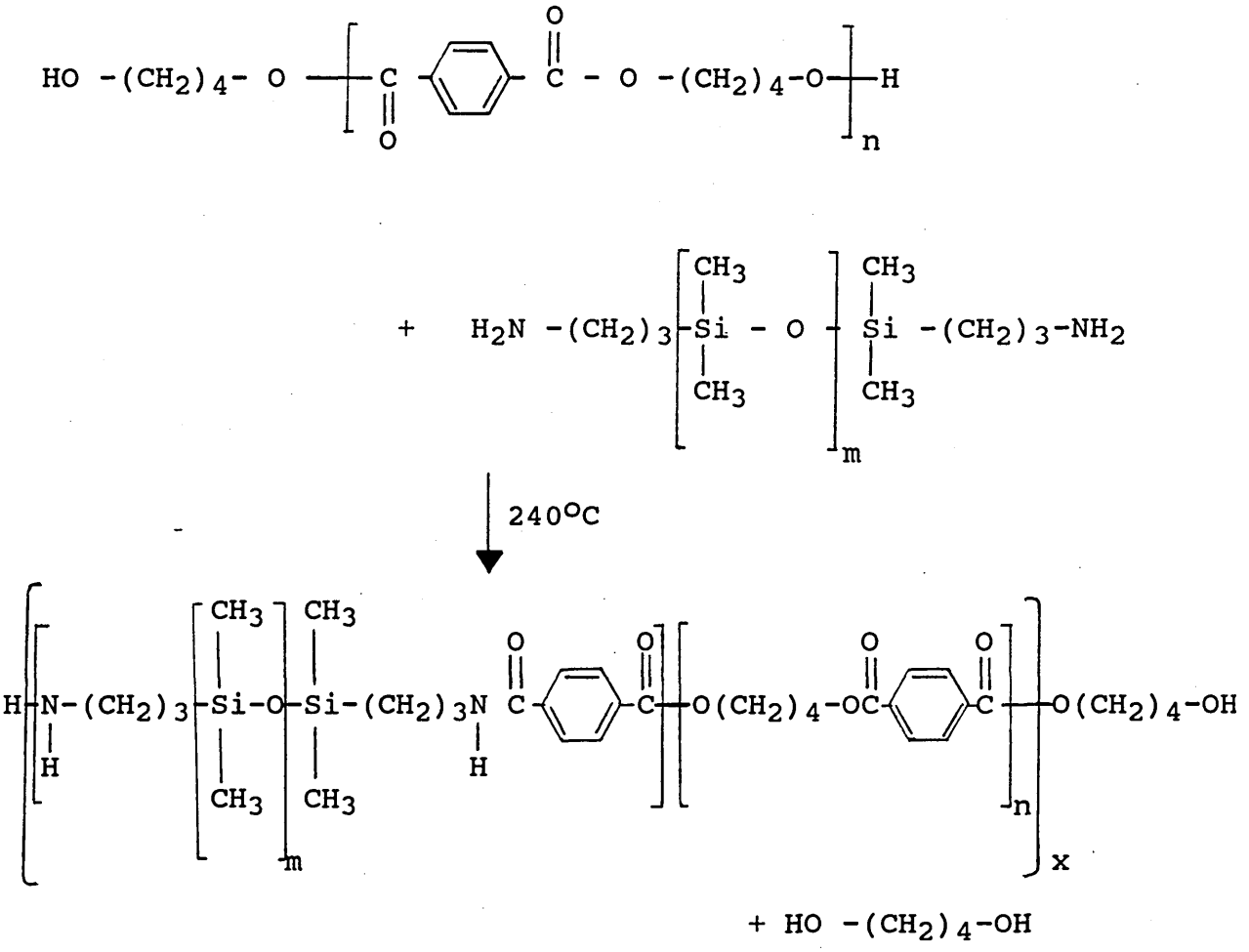


Reaction Scheme 4.3 Preparation of PBT - PDMS Copolymers from the Monomers

Dimethylterephthalate (10g, 0.0515moles), 1,4 Butane diol (6.96g, 0.0773moles) α,ω - hydroxypropyl PDMS(11.8g, 0.0118 moles) and catalyst (tetrabutyltitanate) were added to the reaction flask and heated to 180°C. The reaction mixture was stirred under a nitrogen atmosphere for approximately one hour, before evacuation (to 20 mmHg in thirty

minutes)to remove final traces of methanol. The temperature was raised to 240°C and the pressure reduced to <1 mmHg in approximately fifteen minutes. A polycondensation period of two hours was allowed before filling the flask with nitrogen and removing the sample. A schematic diagram of the apparatus is shown in Fig. 4.1.

4.236 PBT - PDMS Block Copolymer Synthesis via Amidation



Reaction Scheme 4.4 Preparation of PBT - PDMS Copolymers by Amidation

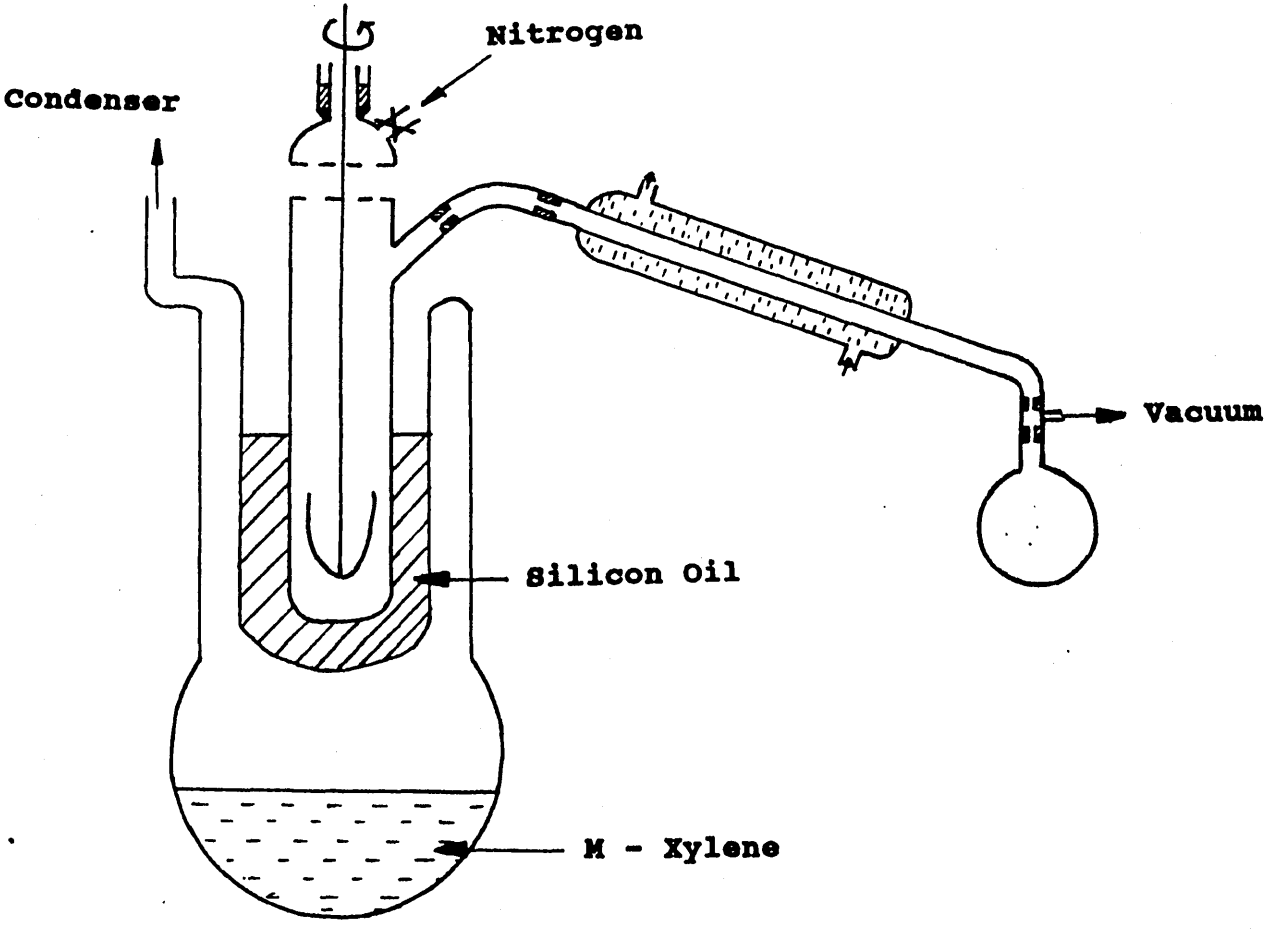


Figure 4.1 Melt Polycondensation Apparatus

PBT α, ω diol (10g, 5×10^{-3} moles) was added to the melt reaction vessel and heated to 240°C in a nitrogen atmosphere. α, ω - amino propyl PDMS (10g, 0.006 moles) was added to the reaction vessel with stirring. The reaction mixture was stirred rapidly for two hours before filling the reaction vessel with nitrogen and removing the product. A number of trials involving these two reactive precursors are reported in Table 4.2.

TABLE 4.2 Reactions of Aminopropyl PDMS and PBT α, ω diol

Sample No	Experimental Details
1	PBT reacted with amine functional PDMS precursor (RMM 1700) at 240°C.
2	PBT reacted with amine functional PDMS precursor (RMM 1000) at 240°C.
3	PBT reacted with amine functional PDMS precursor at 240°C with imidazole catalyst present
4	As (3) but reaction performed at 260°C.
5	As (3) but reaction performed at 280°C.

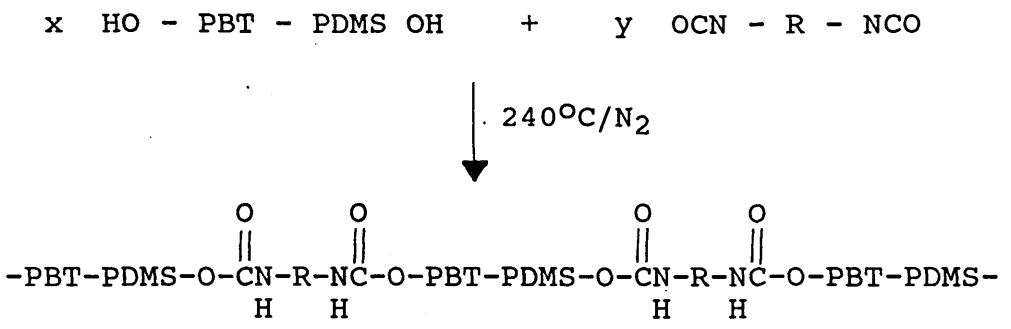
In each case the PBT oligomer was of approximately RMM 2,000 (A8 3102). In sample 1 the amine terminated PDMS precursor was of RMM 1700 while in all other examples PDMS precursor of RMM 1,000 was used.

4.237 Reaction of α, ω Hydroxy PBT with Poly(ethylene glycol) Terminated PDMS

α, ω hydroxy PBT (15g, 1.2×10^{-2} moles) was added to the reaction vessel and melted at 240°C in a nitrogen atmosphere. α, ω poly(ethylene glycol) PDMS (16.8g, 1.2×10^{-2} moles) was slowly added to the reaction vessel with stirring. The reaction mixture was stirred rapidly for two hours before filling the polymerisation tube with nitrogen and discharging the product. The product was subjected to soxhlet extraction with toluene. The resulting fractions were analysed by I.R. and ^{1}H NMR spectroscopy.

4.238 Reaction of Low Molar Mass PBT - PDMS Block Copolymers with a Diisocyanate

Low molar mass PBT - PDMS block copolymer (15g, 0.006 mol) (produced by transesterification route utilising stannous octoate as catalyst) was added to the polymerisation vessel and heated to 240°C in a nitrogen atmosphere. Diphenyl methane 4, 4 Diisocyanate (MDI) (1.81g, 7.2×10^{-3} moles) was added slowly with caution to the copolymer with stirring. A further fifteen minutes were allowed before discharging the reaction product.



Reaction Scheme 4.5 Copolymer Formation using Diisocyanates as Coupling Agents

4.3 Results and Discussion

4.31 Solvent Reactions

As previously described the Hildebrand solubility parameters for the two precursor components for block copolymer formation indicate gross incompatibility. Although this large difference ($\sim 6.6(MJm^{-3})^{1/2}$)would be advantageous from the point of view of promoting microphase separation in the resultant copolymer, the possibility of finding a single solvent which would dissolve both components simultaneously proved to be difficult.

Initial investigations concentrated on using chlorobenzene ($\delta = 19{\cdot}4(MJm^{-3})^{1/2}$) a solvent successfully employed by Noshay et al (136) in copolymerising polysulphone ($\delta = 21.1(MJm^{-3})^{1/2}$) with PDMS. At ambient temperatures chlorobenzene showed no affinity for PBT, not even the low molar mass oligomers. At temperatures approaching its boiling point (132°C) a homogeneous solution of PDMS and low molar mass PBT oligomers (RMM < 2,000) was obtained.

The product obtained on cooling was a white waxy solid whose ^1H NMR and I.R. spectrum revealed characteristics both of siloxane and PBT. Soxhlet extraction of the product with toluene indicated formation of a physical blend of the two components as selective solubilisation of the PDMS phase occurred. The residue proved to be predominantly PBT (by spectroscopy). The solute however, proved to be mainly PDMS, although spectral signals

characteristic of PBT were present. This was probably due to the PBT sample having a broad RMM distribution with the low RMM species being soluble in hot toluene.

1, 2 dichlororobenzene ($\delta = 20.5(MJm^{-3})^{1/2}$) was evaluated as a possible solvent for the copolymerisation, since it had proved to be a successful medium in the copolymerisation of polyethersulphone and PDMS block copolymers (196). It too only showed an affinity for PBT when approaching its boiling point (178^{o}C) and a homogenous solution was obtained with PDMS near this temperature. However, selective solubilisation of the PDMS phase with toluene confirmed the resulting product to be a physical blend of the two components. Other common solvents investigated e.g. Dimethylsulphoxide (DMSO), tetrahydrofuran (THF) and dimethylformamide (DMF) were all found to dissolve one of the oligomers whilst having little or no effect on the other.

Since a suitable single solvent was not found for the copolymerisations, further copolymerisations were attempted in multicomponent solvent mixtures eg. toluene and N - methyl - pyrrolidone (NMP) were investigated. NMP has been reported (194) as an effective medium for poly(arylene ether sulphones) and PBT above 150^{o}C (192) and was found to give homogeneity when used for attempted vinyl functionalisations of PBT. Unfortunately the reaction product was found to be a physical blend of PDMS and PBT.

Another multicomponent solvent system investigated was tetrachloroethane /nitrobenzene (99 5/0.5) since it is a known solvent for PBT at elevated temperatures (191). At ambient temperatures a cloudy solution of PBT was obtained. On heating, an "optically" clear solution formed at approximately 80°C. PDMS and catalyst were added and the reaction allowed to proceed. On cooling a cloudy solution formed. The reaction product was a discoloured solid softer than the original PBT. DSC analysis of the product (Fig. 4.2) showed characteristics of both PBT and PDMS and the I.R. spectrum indicated no Si - H present. Encouragingly some solubility was exhibited using chloroform and a ^{1}H NMR showed characteristics of both components. Soxhlet extraction of the reaction product with toluene yielded extracted material which was an off-white soft solid. DSC analysis of the extracted product (Fig.4.3) showed thermal transitions characteristic of siloxanes and a melting endotherm at 200°C which could be assigned to PBT. The DSC trace also shows a glass transition (Tg = ⁻123°C), cold crystallisation and melting endotherm characteristic of siloxanes. One possible explanation for this is that some siloxane remained unreacted. This would be extracted by the toluene, and give the thermal transitions observed. However, this is unlikely since linear PDMS samples with Mn < 2,000 have been shown to be mainly amorphous materials

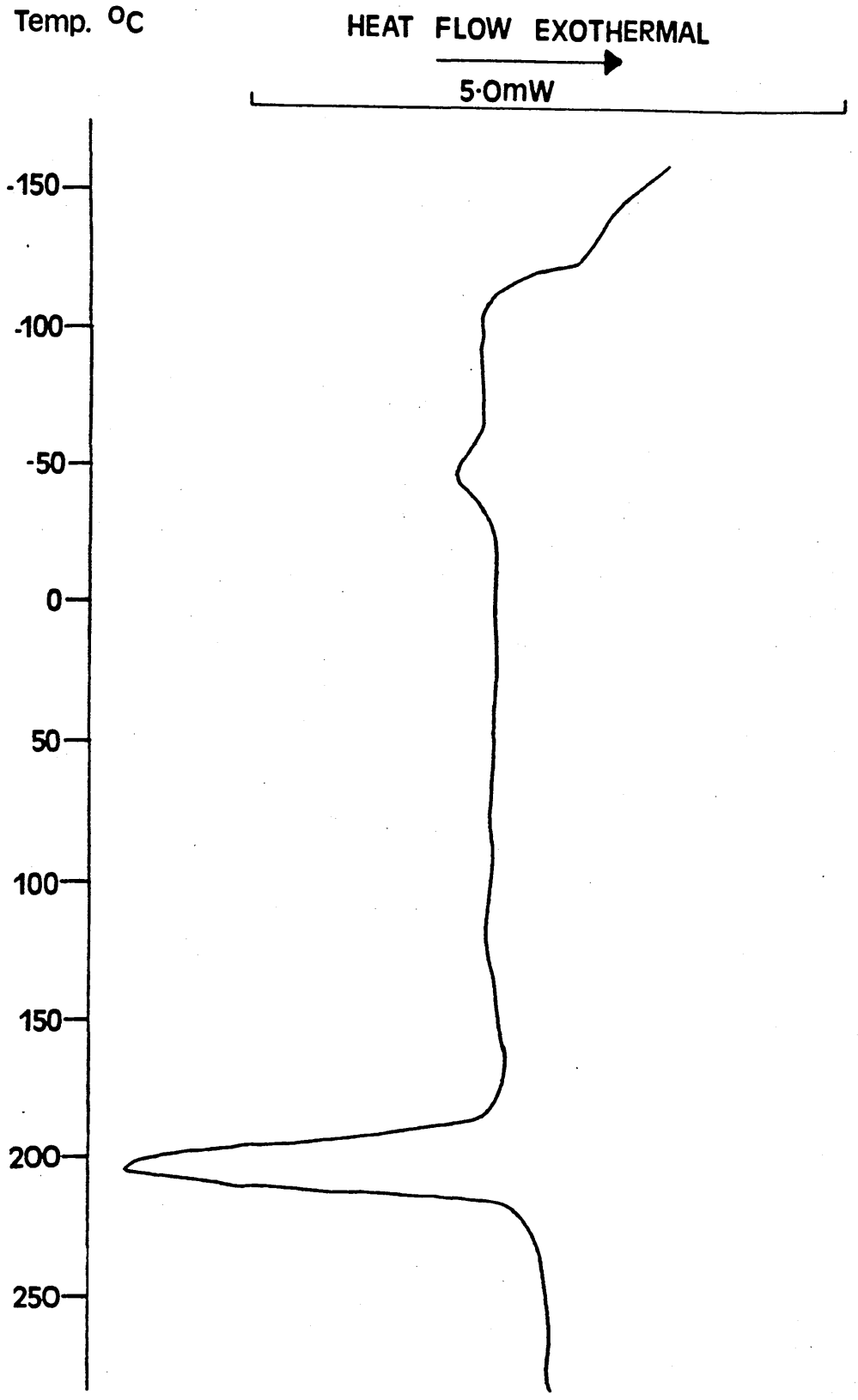


Figure 4.2 DSC Analysis Of Crude Reaction Product From PBT/PDMS Hydrosilation Solution Reaction

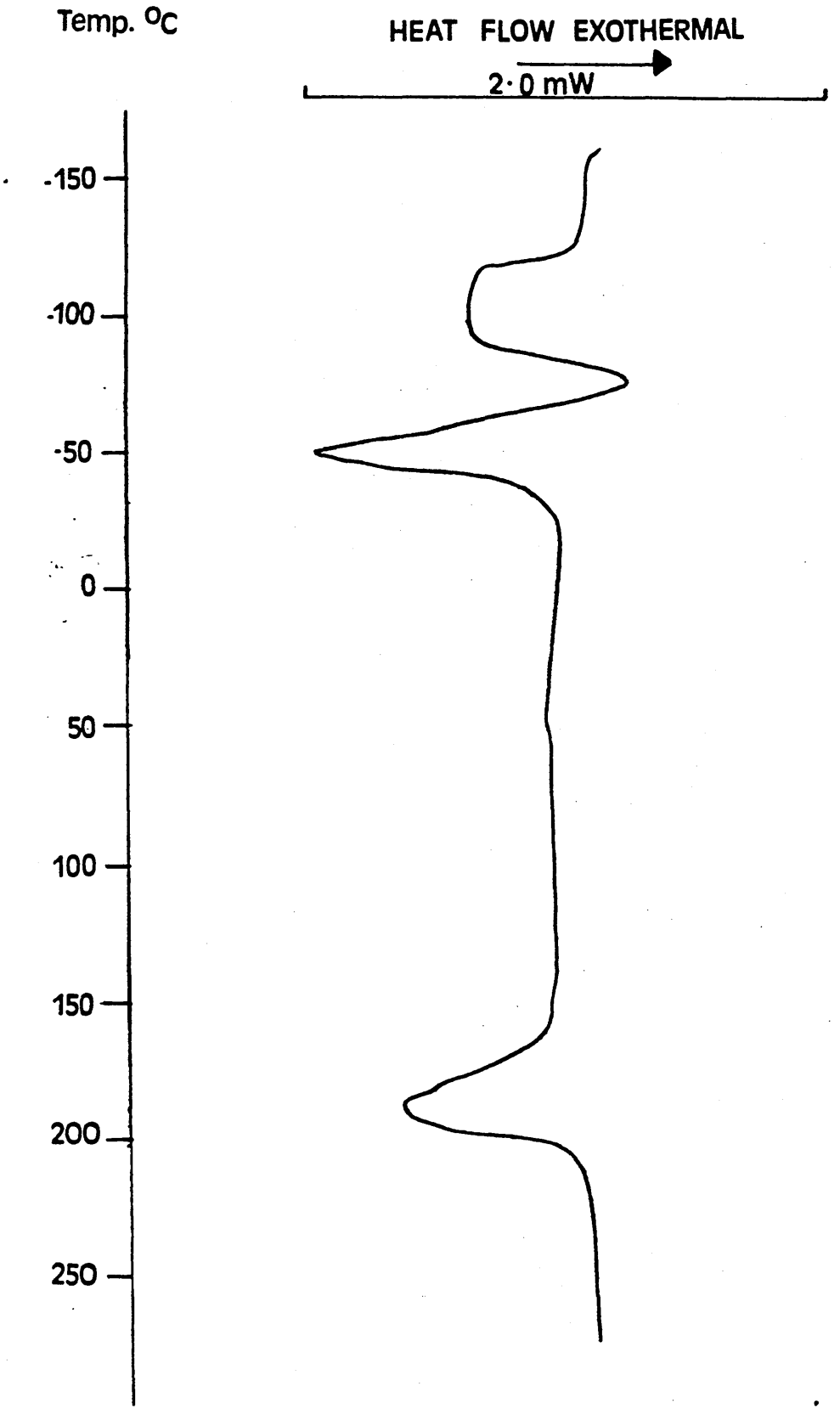
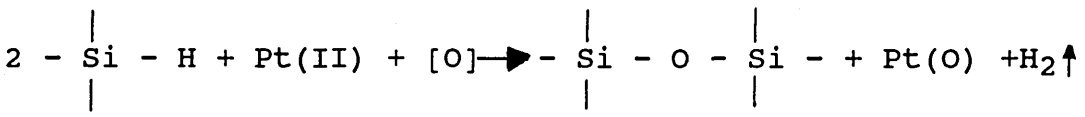


Figure 4.3 DSC Analysis Of Extracted Product From PBT/PDMS Hydrosilation Solution Reaction

(197) giving only a glass transition. Furthermore, polyethersulphone - PDMS block copolymers with moderate molar mass oligomers (~ 3,000) only a glass transition for PDMS was reported (134).

A more feasible proposition is that together with limited copolymer formation a competing reaction of the self condensation of the Si - H functional groups occurs . This gives higher RMM siloxane species, which show similar thermal characteristics.



Reaction Scheme 4.6 Reduction of Si - H end groups (198)

Experiments carried out with tetramethyl disiloxane and hexachloroplatinic acid show the siloxane to reduce the catalyst to platinum metal. When tetrachloroethane is added to this system the rate of reduction is appreciably faster. Therefore, it would seem that tetrachloroethane is not a suitable medium for the hydrosilation reaction since it accelerates the rate of reduction of Pt(IV)→ Pt (0).

A further synthetic route which was investigated was the use of high boiling solvents as compatibilising media for initial PBT - PDMS reactions. The theory is that the necessary amounts of solvent are added to the two incompatible materials to obtain an homogeneous solution. As the reaction progresses excess solvent is removed while

maintaining homogeneity, eventually leaving a compatible bulk system in which more siloxane - PBT interactions could occur. Perec and Auman (134) used this procedure in the synthesis of PES - PDMS block copolymers.

Solvents investigated for this purpose were biphenyl ether, 1 - chloronapthalene, sulpholane and a two component solvent system of tetrachloroethane and nitrobenzene (99.5/0.5).

The three high temperature solvents were each added in small volumes to the melt system containing PBT and PDMS and stirred vigorously. However, none of these proved successful in overcoming the incompatibilty problem, phase separation occurring when agitation was stopped.

Tetrachloroethane/nitrobenzene (99.5/0.5) was used in a dilution-concentration type block copolymer synthesis, the reaction being carried out in a similar apparatus to that shown in Fig. 4.1. m-Xylene was used as the vapour bath.

The reaction mixture was initially homogenous. The reaction was allowed to proceed gradually removing solvent by periodically applying vacuum to the system. However, a point was reached where the system began to show slight inhomogeneity. The reaction was allowed to proceed for a further six hours but unfortunately the slight inhomogeneity remained. The product was isolated by precipitation from slightly acidified methanol. The

product proved to be a blend when subjected to soxhlet extraction with toluene.

4.32 Melt Reactions

Since solvent systems were found to be unsuitable for providing a suitable media for the block copolymerisations, melt reactions were investigated. Thermoplastic elastomers composed of segmented copolyether-esters have been successfully synthesised by this technique (168), using oligomers of suitable of RMM (< 2,000). Trials were therefore carried out to synthesise PBT - PDMS copolymers using low RMM functional oligomers attempting block copolymer formation by a number of different chemical routes.

4.321 Esterification Reactions

One of the earlier melt reactions attempted was esterification between α, ω hydroxy PBT and α, ω - bis (10 - carboxydecyl) PDMS. Bis(10 - carboxydecyl) PDMS was chosen as 10 - undecenoic acid had previously been shown to react successfully with α, ω hydroxy PBT at 240°C. A further possible advantage , as previously mentioned, was the presence of the 10 methylene groups linked to the siloxane backbone. These may enhance compatibility towards PBT.

Unfortunately, this route proved unsuccessful. The product obtained was a soft white solid which appeared to be a dispersion of PBT throughout a PDMS matrix. The product was subjected to soxhlet extraction using toluene as

solvent. A powdery solid remained insoluble in the toluene an was shown to be PBT (by I.R.) in which the hydroxyl group had not reacted significantly. The material extracted into the toluene proved to be PDMS (^{1}H NMR). It would appear that little or no reaction occurred and only a physical blend was obtained during stirring. The incompatibility of the two polymers probably limited the number of interactions of the mutually reactive end groups to a minimum, therefore ensuring little or no reaction.

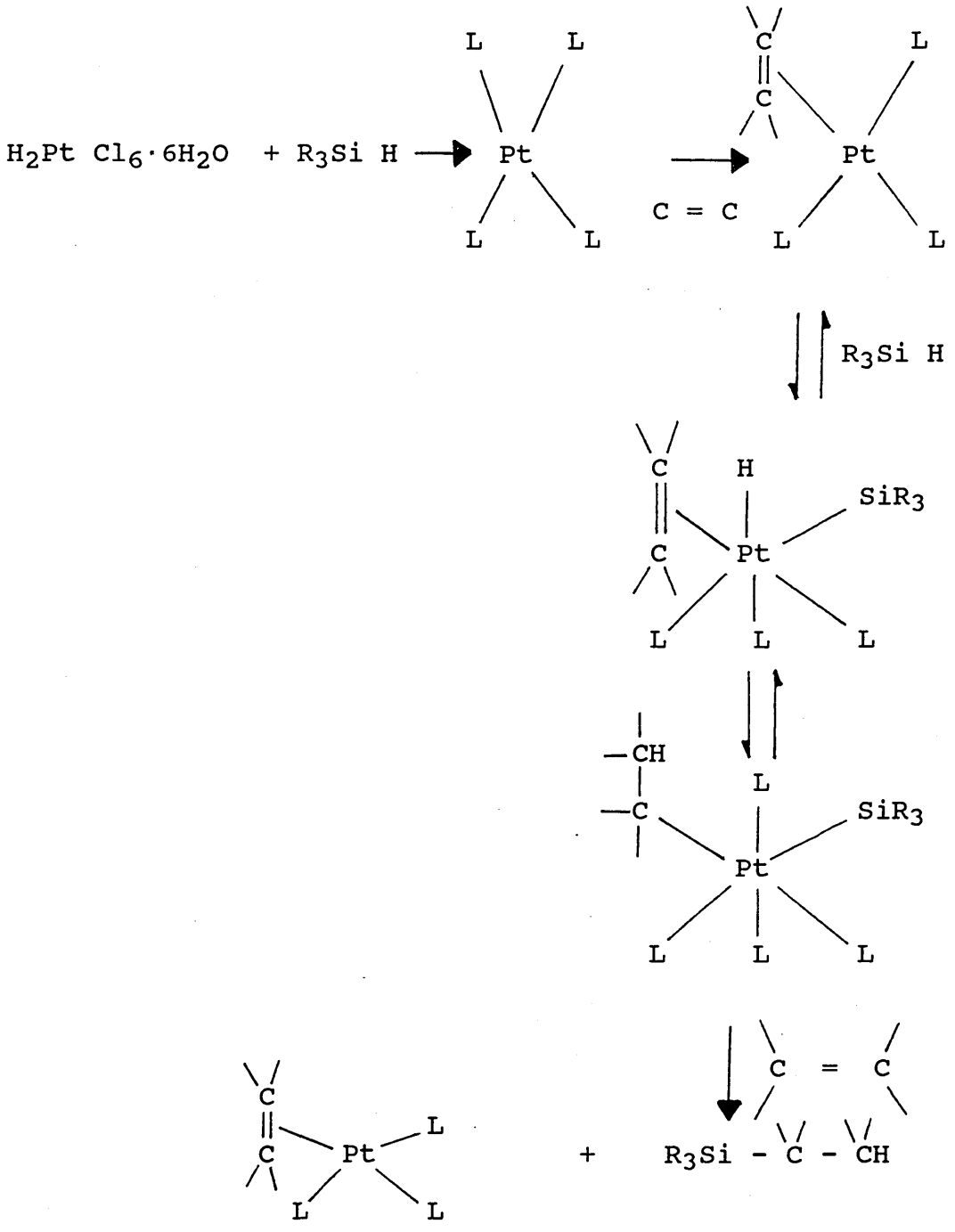
The reaction was also performed with α, ω - carboxypropyl PDMS of relative molar mass of approximately 1,000, as the functional siloxane oligomer. This reactive system also failed to clear and the reaction product was found to be a blend. It appears even when using lower RMM siloxane oligomers that the incompatibility of the block precursors restricts the potential esterification reaction of the end groups.

4.322 Hydrosilation Route

The hydrosilation route linking hydride terminated PDMS with vinyl terminated PBT was initially performed using vinyl terminated PBT. This was synthesised by using triethyleneglycol phosphoric acid to deactivate any titanate catalyst present. This method has been shown to give approximately 80% conversion of hydroxyl groups and the terminal vinyl groups were unaffected by the catalyst.

Several trials were carried out using vinyl terminated PBT and α, ω di(hydrosilane) with varying results. In the early trials the product obtained was dark grey in colour. This colouration could be explained by ageing of the catalyst. The chloroplatinic acid solution in THF used was about fourteen days old. Pt(IV) is gradually reduced to Pt(II) in solution (199). Therefore, the mechanism which is proposed for the hydrosilation reaction (125,200) (see scheme 4.7), was probably no longer appropriate. It is only likely to be appropriate when using freshly prepared solutions of hexachloroplatinic acid, when the catalytic species would be mainly $Pt\ Cl_6^{2-}$.

However, in the aged catalyst most of the Pt is likely to be in the form of Pt(II). Reaction with the Si - H end groups of PDMS results in finely divided Pt metal being produced (201). This finely divided platinum is probably the most likely cause of the colour of the product prepared



Reaction Scheme 4.7 Hydrosilation mechanism for chloroplatinic acid.

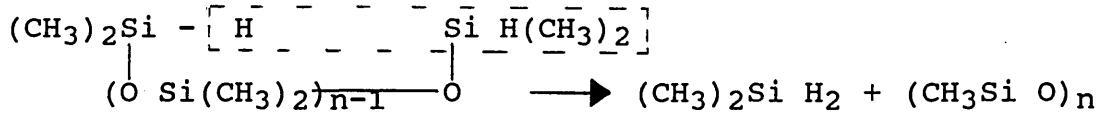
L = unspecified ligand, presumably chlorine, hydrogen or coordinated solvent.

using the aged catalyst. Additional evidence of the reduction of Pt(IV)⟶Pt(II) is that when the catalyst was added to the hydride terminated siloxane, effervescence occurred and a yellow colouration developed. Addition of a freshly prepared catalyst solution does not result in such observations. The explanation of this phenomenon is that the Pt(II) species catalyses the reduction of Si - H end groups to liberate hydrogen (198) (Reaction Scheme 4.6). (Gray et al (202) experienced similar problems when preparing liquid crystalline polysiloxanes obtaining coloured products when using aged catalysts). In later block copolymerisation trials freshly prepared catalysts were used in all cases and white or cream coloured products were obtained when reaction periods of one hour or less were used.

Also in the initial trials as well as grey coloured products the products became very viscous at 230^{o}C which could indicate crosslinking. However, this would be more likely if the hydride functions were along the siloxane backbone rather than at the ends of the siloxane chain. Another explanation is that a block copolymer with a high relative molecular mass has been formed. However, this is unlikely since for the preparation of high RMM block copolymers it is necessary that a $\bar{F}n$ = 2.0 (ie. 2 functional groups per chain) be maintained. This is difficult to acheive since although equal stoichiometric amounts of reactants are present initially, the hydrosilation reaction is known to undergo some side

reactions. These consume Si - H and thereby decrease the functionality of the α,ω di(hydrosilane) PDMS.

The Si - H can be consumed by a redistribution reaction in the presence of Pt complexes, in which an internal SiO/H exchange occurs, (203,204).



Reaction Scheme 4.8 Redistribution Reaction by an Internal SiO/H Exchange.

Also possible is the platinum catalysed disproportionation of hydrosilanes (205) which would reduce the Si - H end groups concentration.

Vinyl terminated PBT contains as well as terminal vinyl end groups, a small proportion of hydroxy end groups, carboxylic acid end groups and methyl ester end groups as complete vinyl functionalisation did not occur. The hydroxy and carboxylic acid end groups may undergo side reactions with the Si - H group (182). This further detracts from the possibility of a high RMM PBT - PDMS block copolymer being formed, as it is difficult to maintain a $\bar{F}n = 2.0$.

However, usually the side reactions of Si - H are much slower than the desired addition reaction (206) for block formation. Thus if the rate of addition is much faster than the side reactions this method should be suitable for block copolymer synthesis.

A possible explanation for the viscous products is that some hydrosilation occurs but the main reaction is that of reduction of Si - H end groups to form higher RMM PDMS. Evidence for this is that while both Pt(II) and Pt(0) are able to catalyse the hydrosilation reaction, their reactivity and effectiveness differ greatly from that of Pt(IV). For the Pt(II) species the reduction reaction is probably more favoured. An I.R. spectrum of the product revealed no Si - H ($2120cm^{-1}$) present but it was not possible to identify if the terminal vinyl signals had been consumed.

Soxhlet extraction of the products with toluene seems to confirm this. DSC analysis of the material remaining after extraction showed no signs characteristic of siloxanes. The DSC trace of the original product shows evidence of siloxanes being present (Figs. 4.4, 4.5). The ^{1}H NMR of the extracted material showed it to be predominantly siloxane.

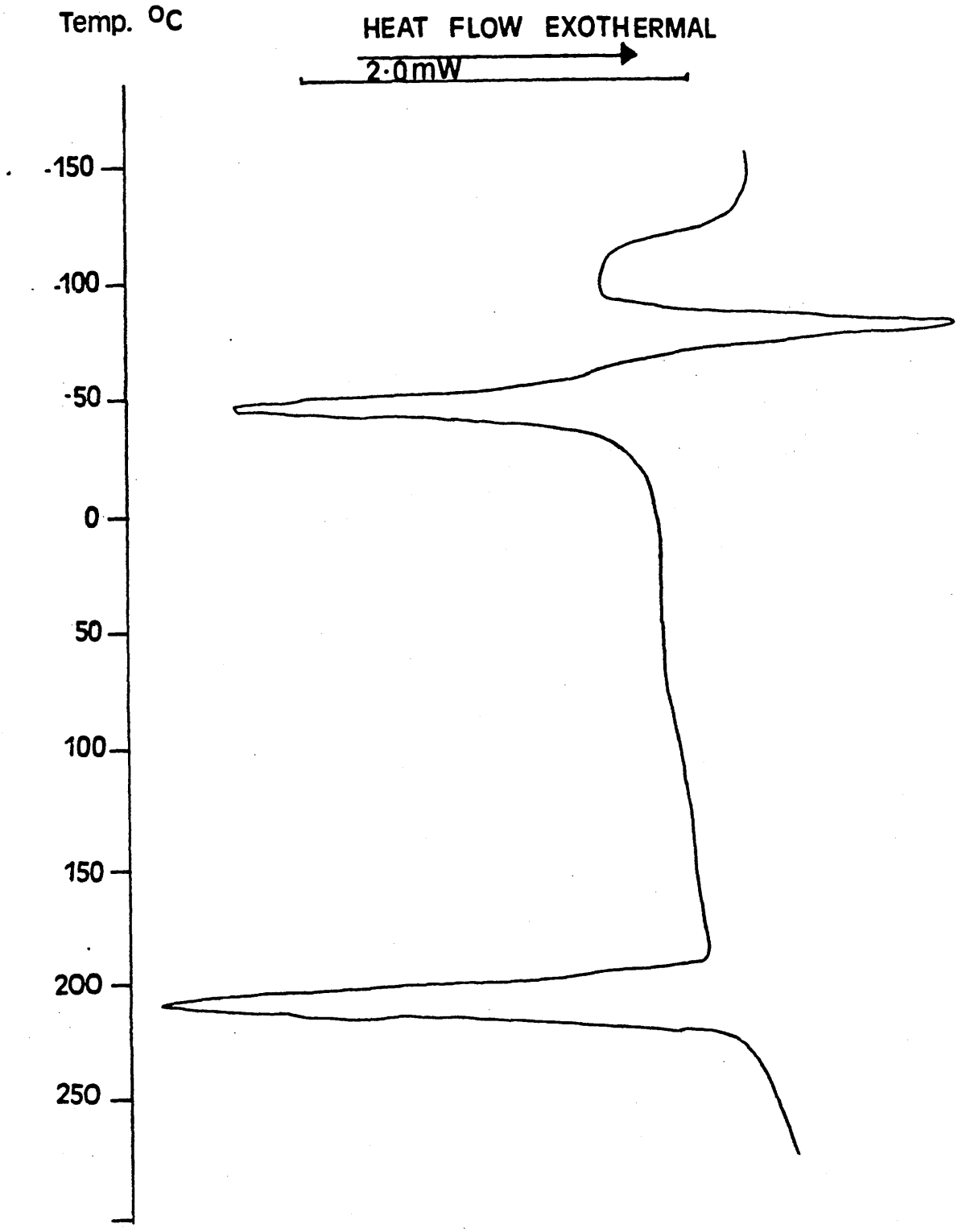


Figure 4.4 DSC Analysis Of Crude Reaction Product From PBT/PDMS Melt Hydrosilation Reaction

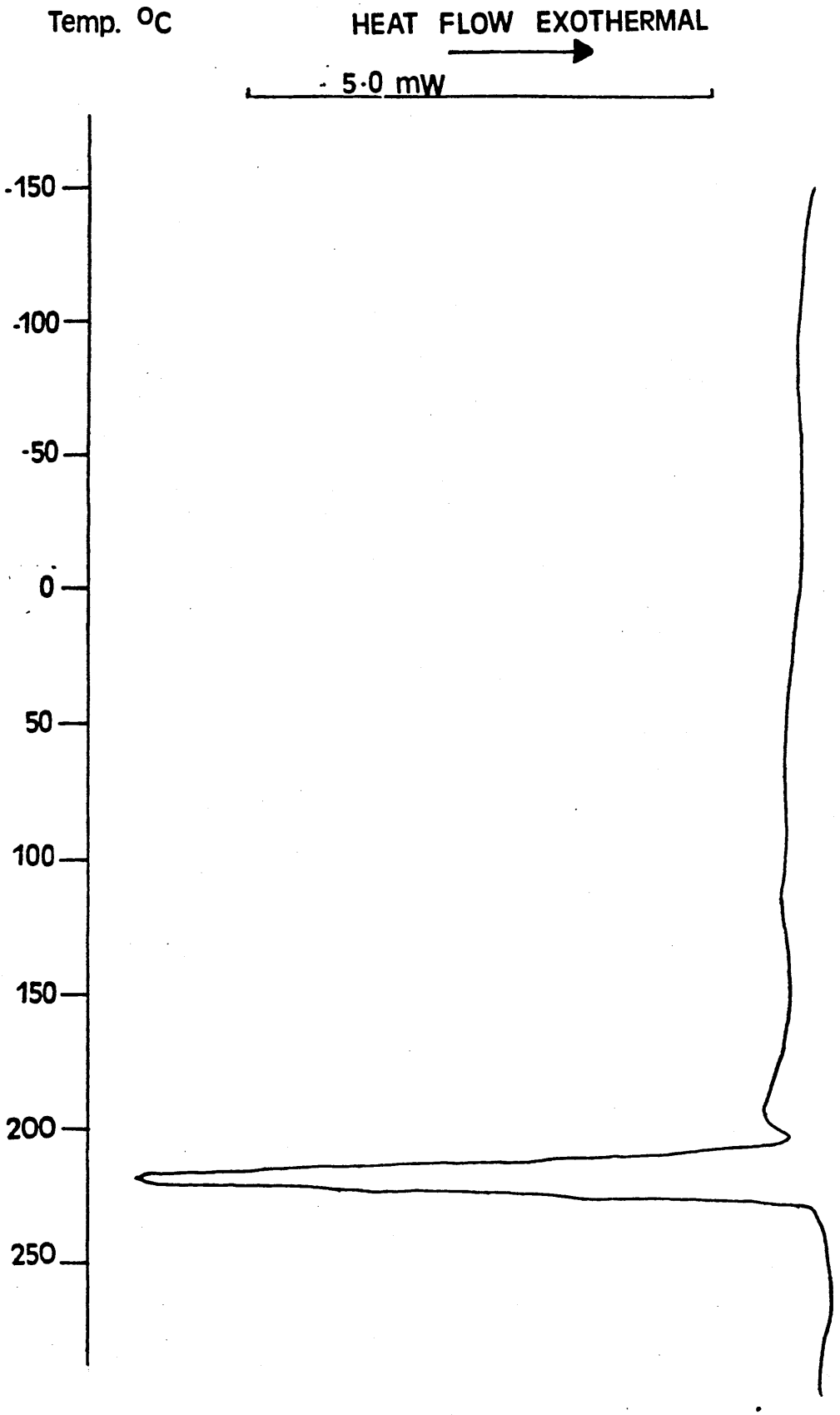


Figure 4.5 DSC Analysis Of PBT/PDMS Melt Hydrosilation Reaction Product Remaining After Soxhlet Extraction

Several further attempts were made to prepare block copolymers by reacting vinyl functionalised PBT with hydride terminated PDMS. The catalyst in each case was freshly prepared and the products obtained were usually off white or cream in colouration. However, although the trials were unsuccessful, usually with soft solids being produced, there were indications that limited reaction was occurring. ^{1}H NMR analysis (270 MHz) showed no vinyl signals or Si - H signals present in the material, which was soluble in deuterated tetrachloroethane. However, the extent of the reaction appeared to be somewhat limited. This is explained by;

(a) The drastic incompatibility of the two polymers.

(b) The ageing of the catalyst.

(c) The side reactions of the Si - H groups.

To detract further from the success of the hydrosilation route were questions concerning the thermal stability of hexachloroplatinic acid. A series of trials were carried out in which the length of reaction times were varied from five minutes to two hours. The products ranged from being brittle solids (reaction time five minutes) through to soft solids (reaction time two hours). Unfortunately none of these experiments produced an elastomeric product initially. However the reaction products were re-examined approximately two to three weeks later when the reaction product which had undergone a reaction period of thirty minutes, showed recovery properties and was the most elastomeric of the materials.

A possible explanation for this phenomenon is that the hydrosilation reaction continues over a long period of time at room temperature. For the trials with reaction time of five minutes the product was a brittle solid, and this is possibly due to insufficient mixing of the two polymers in the short time scale. The trials of one hour or longer produce soft solids which crumble easily, and have virtually no elastomeric properties. A possible reason for this is reduction of the catalyst from its original Pt(IV) to Pt(0) via an intermediate Pt(II) state. Platinum metal is not a very good hydrosilation catalyst and, therefore, the addition across the double bond is unlikely to take place. Further evidence for the oxidation state of the metal is obtained by the grey colouration observed in many of the samples prepared in reactions longer than one hour.

Degradation of the catalyst in the melt was shown to occur when the catalyst was heated with hydride terminated siloxane at 240^{o}C. Two trials were carried out, one with an aged catalyst (> four weeks) and α, ω - dihydrosilane for two hours at 240^{o}C. The other trial used a freshly prepared catalyst and α, ω - dihydrosilane, under the same conditions. Both samples turned black during the reactions. Infrared spectra of the two samples showed their Si - H signals to have decreased to approximately half their original intensity. GPC analysis (Figs 4.6) indicates an increase in RMM (from 2,000 to 10,000) both

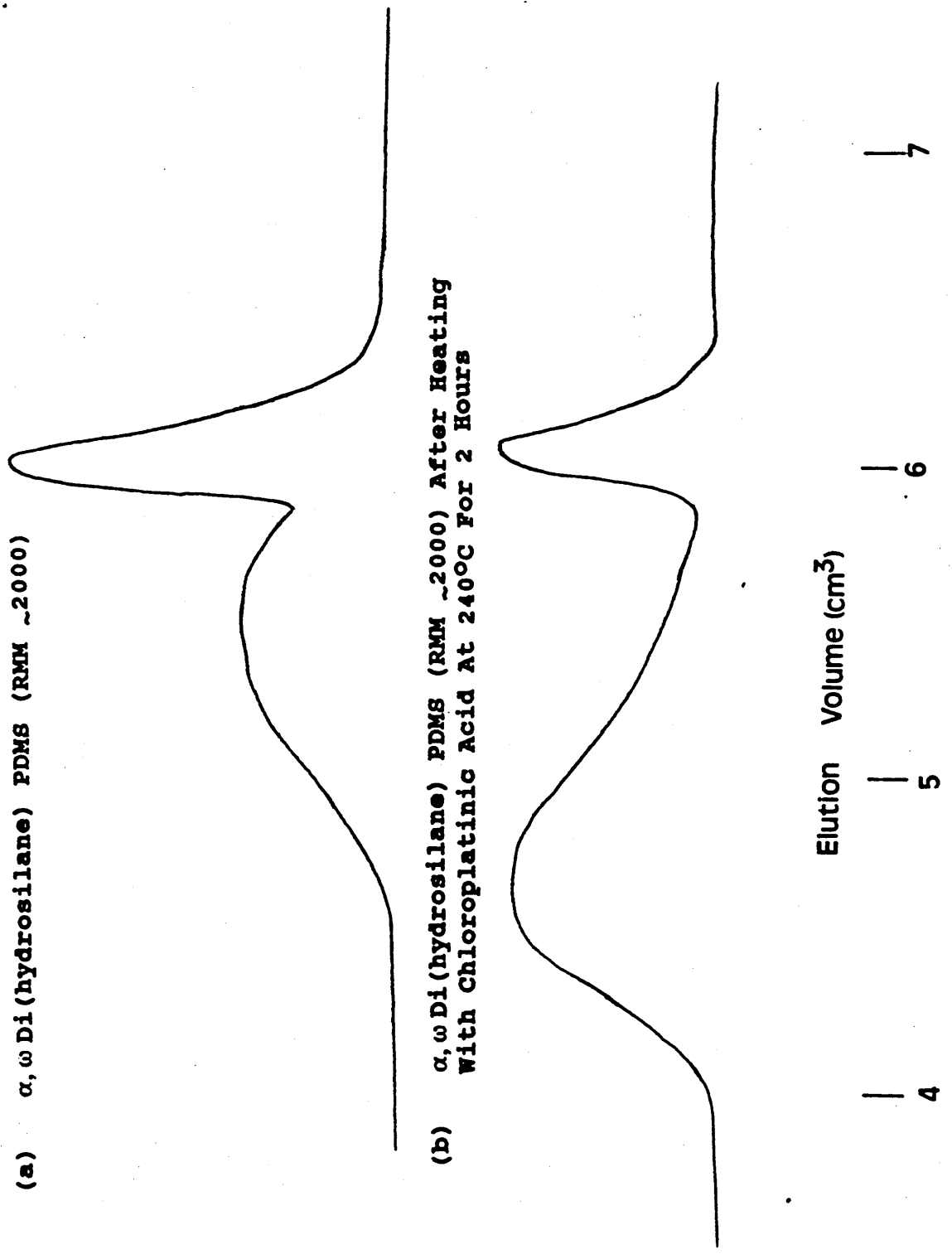


Figure 4.6 GPC Analysis Of α,ω Di(hydrosilane) PDMS

products being of very similar RMM. It appears that Pt(IV) is reduced to Pt(II) in the melt reactions, reducing the effectiveness of the hydrosilation reaction. Further confirmation that the RMM of the PDMS increases during these block copolymerisations is obtained from the DSC traces of the products. It has been shown (197) that above a certain RMM linear PDMS shows four thermal transitions. These transitions are the glass transition, an exothermal crystalline formation (cold crystallisation following supercooling) and two melting endotherms of crystalline forms. It has been reported (197) that with increasing RMM the second crystalline melting endotherm becomes more prominent than the first melting endotherm and this is seen for the products described here.

However, using a system containing only hydride terminated siloxane to assess this thermal stability is inappropriate as there is only a reducing agent present. Therefore reduction of the catalyst would occur with time (201). The degradation study was thus repeated using silicon oil in the reaction system, which is non-functional. Unfortunately after two hours a fine dispersion of black particles was observed. Therefore, it appears that hexachloroplatinic acid is thermally unstable at the melt reaction temperature.

The thermal instability of hexachloroplatinic acid together with unfavourable side reactions of Pt(II) and Pt(0) species suggest that it should no longer be used as the catalyst for this system. Further to detract from its use is the unpredictability of rapid ageing of freshly prepared catalyst solutions, sometimes within twenty four hours.

The thermal stabilities of four other potential hydrosilation catalyst were evaluated. This was performed by heating the catalyst in silicon oil at 240°C in a nitrogen atmosphere for approximately one hour. The catalysts examined were a commercially available material from Wacker (catalyst OL), tris(triphenyl phosphine) rhodium chloride $(Ph_3P)_3Rh\ Cl$, bis(triphenyl phosphine) platinum dichloride $(Ph_3P)_2Pt\ Cl_2$ and bis(isopropyl diphenyl phosphine) platinum dichloride $(Ph_2P\ Pr^i)_2Pt\ Cl_2$.

It was expected that the phosphine ligands would increase the thermal stability of the platinum complexes. Rhodium complexes have been indicated as good hydrosilation catalysts (127) and could be thermally more stable.

The catalyst available from Wacker (catalyst OL)was very unstable thermally at this temperature, imparting a black colouration to the silicone medium almost immediately .

The rhodium complex $(Ph_3P)_3Rh\ Cl$ and bis(triphenyl phosphine) platinum dichloride $(Ph_3P)_2Pt\ Cl_2$ appeared to possess greater thermal stabilities at 240°C. However,

their solubility in silicon oil is limited. Bis(isopropyl diphenyl phosphine) platinum dichloride ($Ph_2P\ Pr^i)_2Pt\ Cl_2$ proved to be soluble in the silicone medium and also thermally stable at 240°C. However, experiments showed it not to be an active hydrosilation catalyst.

The hydrosilation route to PBT - PDMS copolymer synthesis under melt conditions proved unsatisfactory. The incompatibility of the polymers, the side reactions of the Si - H end groups together with the instability of active hydrosilation catalysts caused this synthetic route to be discontinued.

4.323 Transesterification Reactions

A number of thermoplastic elastomers composed of segmented copolyether-esters are now commercially available (168). Their composition can be described as an $-[-A-B-]_n-$ structure, where A represents a polyether segment and B a polyester segment. In most cases the polyether segment A is derived from a hydroxyl terminated aliphatic polyether e.g. α,ω hydroxy poly(oxyethylene). The polyester segment B is usually a rigid high melting aromatic polyester derived from terephthalic acid. The preparation of these materials is based on the ester-interchange reaction as is well known for the preparation of poly(ethylene terephthalate) (PET) and PBT (207). It was hoped that by replacing the aliphatic polyether portion with a α, ω hydroxy PDMS a segmented copolysiloxane-ester could be produced.

Many trials were carried out using α, ω hydroxy PBT oligomers of RMM approximately 2,000 together with α, ω hydroxypropyl PDMS oligomers of RMM 1,000 and 1,800 respectively. The use of hydroxypropyl PDMS oligomers ensured Si - C links throughout any copolymer product.

The trial reactions involving the higher RMM siloxane precursor proved unsuccessful, an immiscible blend being obtained. However, the experiments using the lower molar mass siloxanes did prove to be successful. The reaction system consisting of 50% m/m (mass/mass) PBT and 50% m/m PDMS is initially white, which is characteristic of an immiscible blend, and remains so until an hour reaction period had elapsed. After this time the reaction mixture started to become translucent and as time progressed the system became clearer but never achieved complete transparency. After approximately ninety minutes a vacuum (<10 mmHg) was applied for approximately ten minutes. On releasing the vacuum an optically clear reaction mixture was obtained. On cooling a white elastomeric, homogeneous product was obtained.

Subsequent analysis indicated block copolymer formation. A ^{1}H NMR (Fig. 4.7) and I.R. spectrum (Fig. 4.8) of the product show siloxanes and PBT segments to be present. The

Figure 4.7 ^1H NMR Of PBT-PDMS Block Copolymer

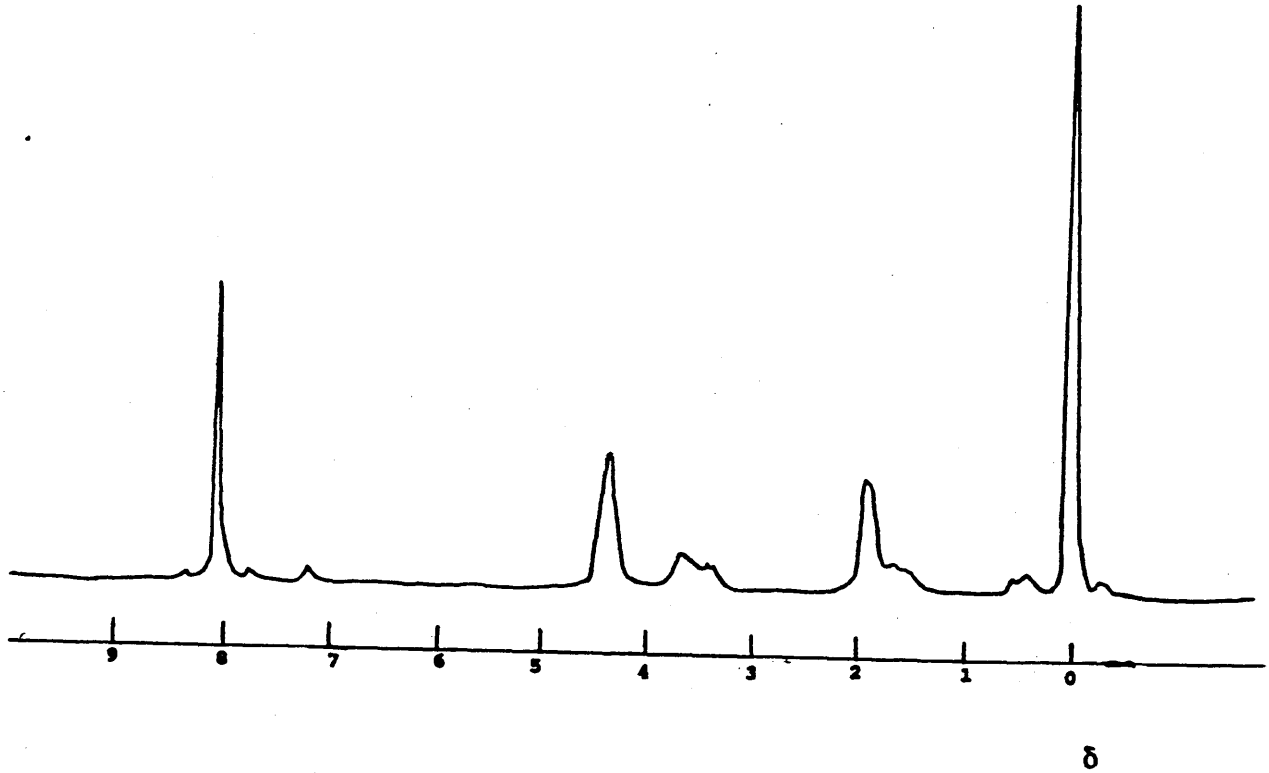
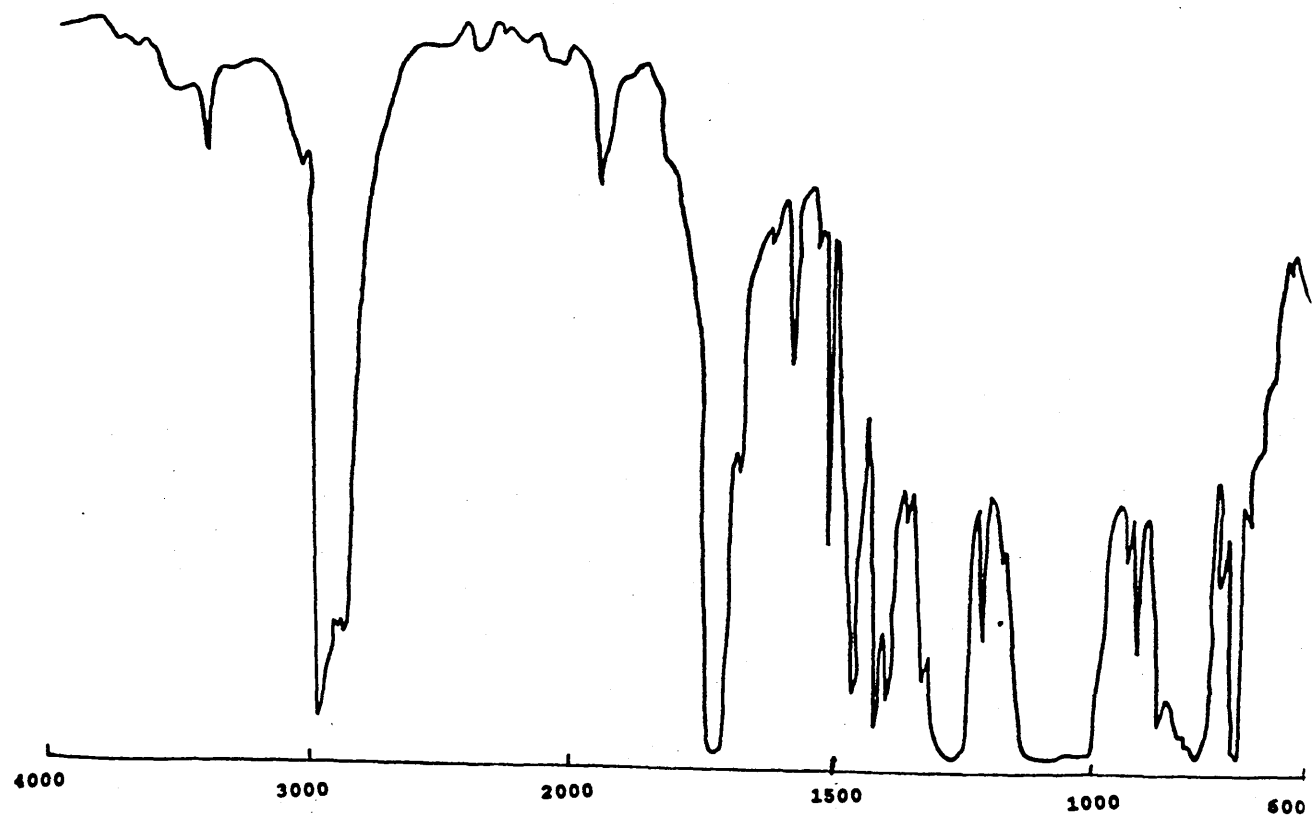


Figure 4.8 I.R. Spectrum Of PBT-PDMS Block Copolymer



I.R. spectrum shows that the number of hydroxyl groups present have significantly decreased when compared with the starting materials.

Further evidence to confirm that a copolymer has been formed is obtained by thermal analysis. DSC data for the copolymer and the PBT oligomer precursor are shown in Table 4.3.

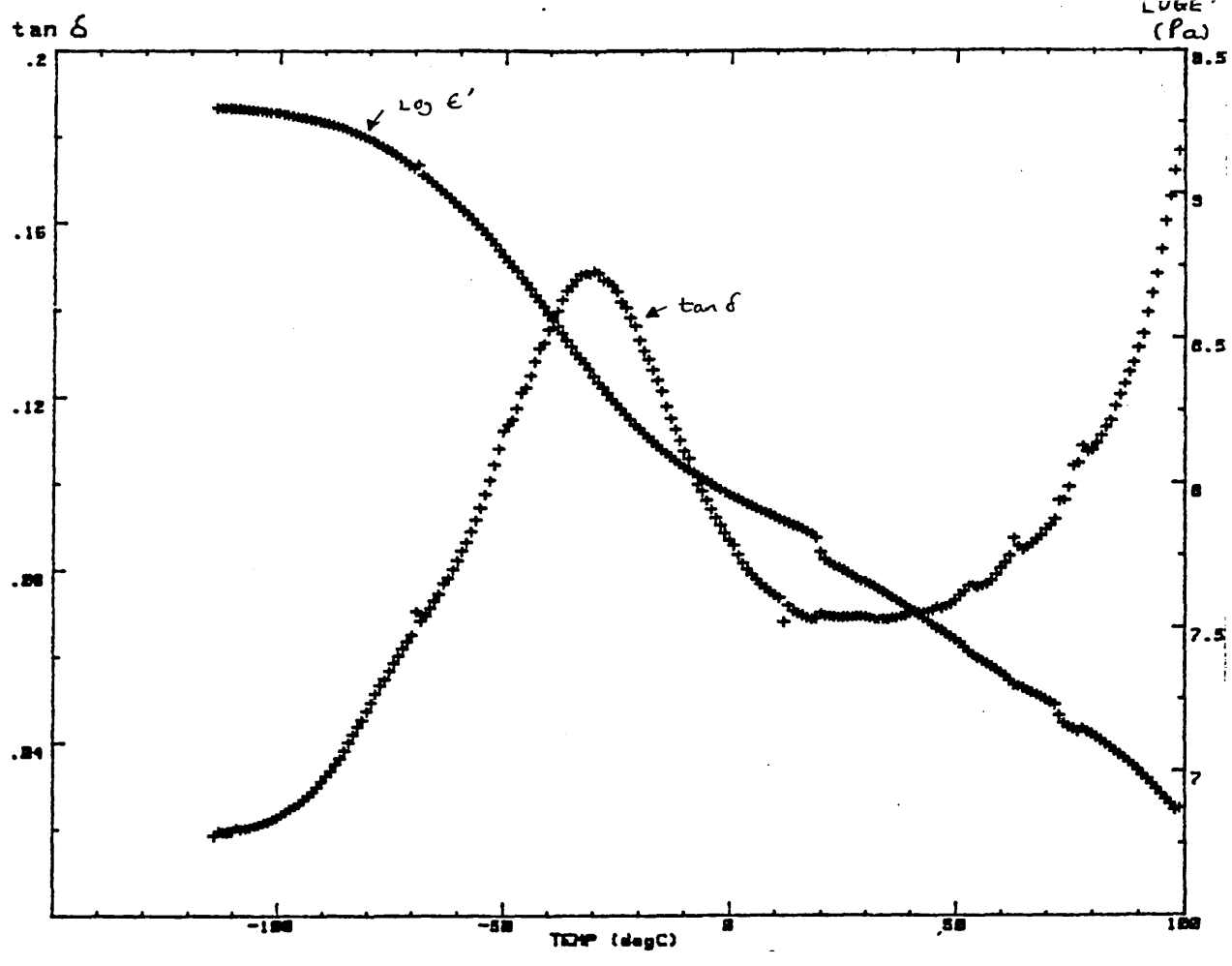
TABLE 4.3 DSC Data for PBT and PBT - PDMS Block Copolymer

Sample	ΔH J/g	Melting Endotherm Peak Temp / ^{o}C
PBT	63.21	215
Copolymer	27.23	184

N.B. ΔH value per g/copolymer.

In Table 4.3 the melting endotherm peak of PBT has been reduced by almost 40^{o}C in the reaction product. This is explained by the chemical attachment of siloxanes to PBT segments. This also affects the enthalpy of crystallisation since the crystalline packing of the PBT chains is disrupted on chemical modification.

DMTA analysis of the copolymer gave a single broad glass transition around - 30^{o}C (tan δ max) as illustrated in Fig. 4.9. As the soft (PDMS) and hard domains (PBT) are relatively small, the PDMS - PBT copolymer does not show the separate glass transitions for each of the soft and hard segments. Separate Tg's are characteristic of a block copolymer having much longer segment lengths (118).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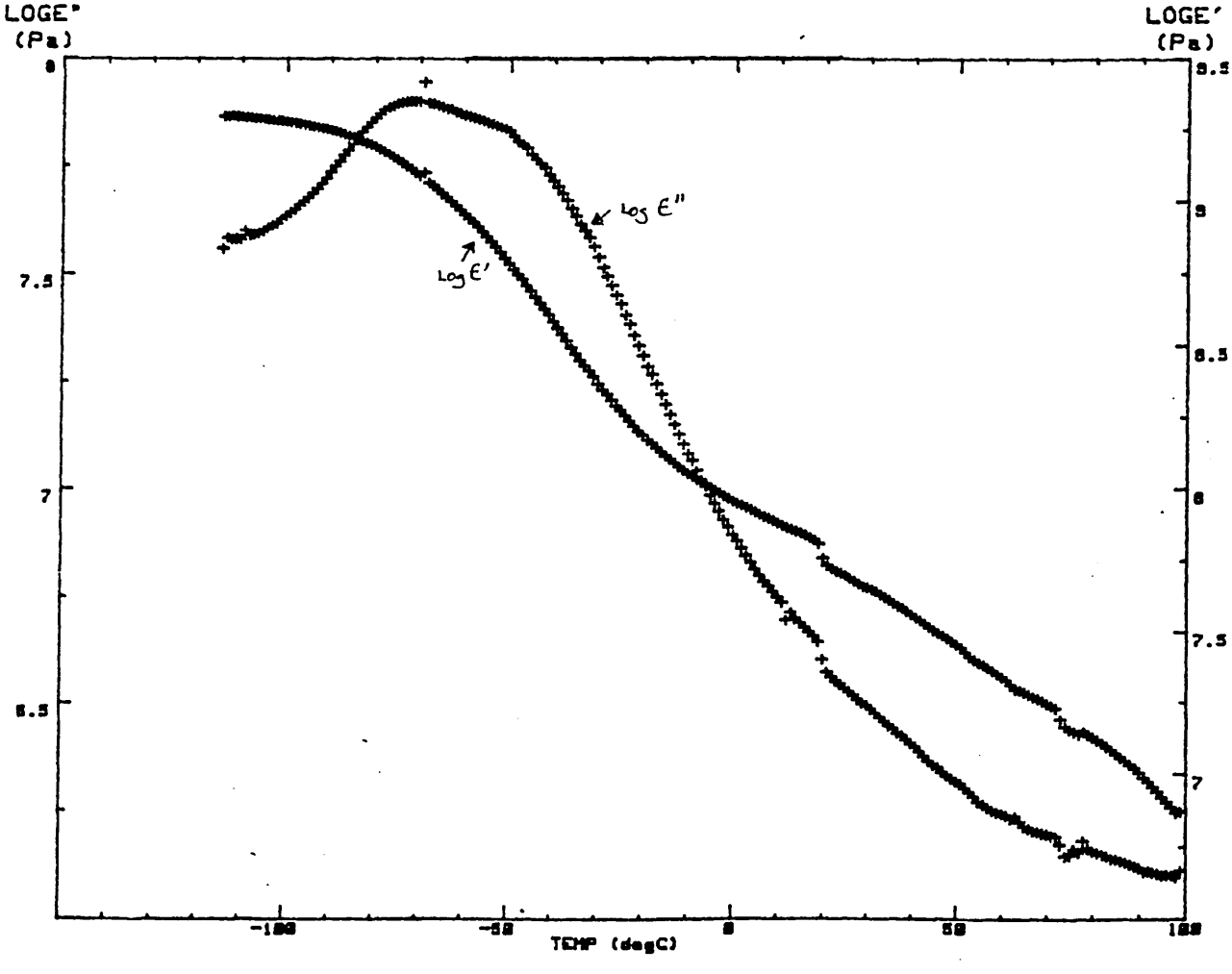
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Unfortunately a problem with the copolymer is that it has an RMM (Mn 2495(VPO)) too low to be of use as an engineering plastic. Further trials were carried out in order to optimise block copolymer formation. These included altering such parameters as, RMM of precursors, catalyst choice and polycondensation period.

Stannous octoate was used as the catalyst initially, although it was expected that titanium based catalysts would be more effective than tin(II) as a polycondensation catalyst, since they are used extensively in the preparation of PBT (159). Tetraisopropyltitanate $Ti(O^{i}Pr)_4$ and tetrabutyltitanate $Ti(OBu)_4$ were chosen as catalysts for this system.

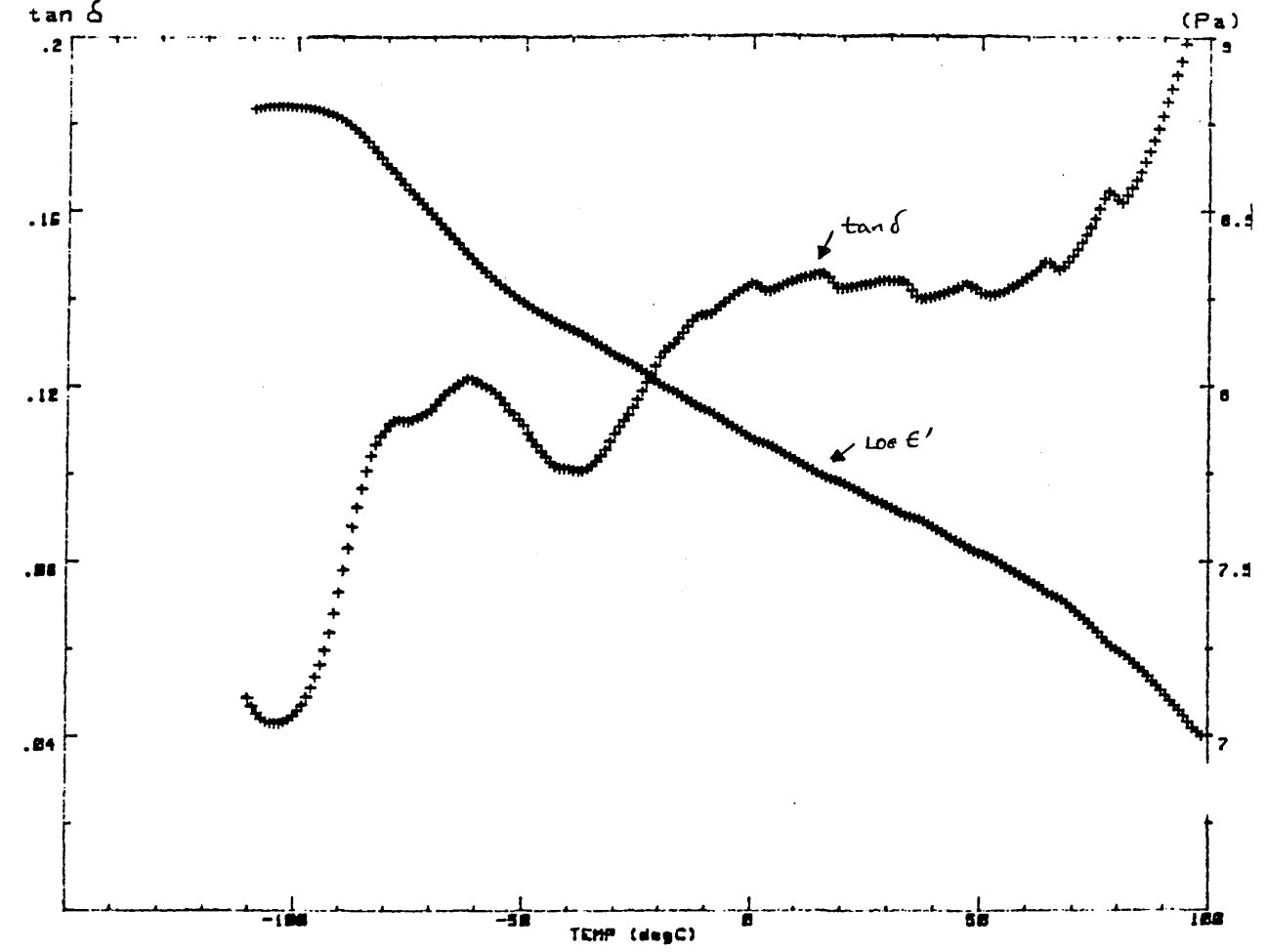
Initial trial reactions involved $Ti(O^{i}Pr)_4$ which was added to the PBT (2,000) - PDMS (1,000) reaction mixture and then after a short period of stirring (five to ten minutes) the pressure was reduced to 0.1 mmHg over approximately fifteen minutes. Although the viscosity increased the system failed to clarify after ninety minutes. However, using this procedure stannous octoate also failed to produce a clear reaction mixture. It is assumed that the two separate components were still not completely miscible using a short mixing period before applying vacuum. This probably results in transesterification occurring predominantly between the PBT segments.

In the trials that followed a mixing period of one hour was usually allowed before reducing the pressure in the system. When $Ti(OBu)_4$ or $Ti(O^iPr)_4$ were used as catalysts the viscosity increased during the initial mixing period, but the mixture remained white. Reduction of the pressure for two hours did not facilitate the system becoming homogenous.

Both products obtained after being subjected only to mixing for one hour and both mixing and application of a vacuum programme were white solids with poor mechanical properties. Compression moulded samples of both products crumbled on attempted removal from the mould.

Fortunately DMTA analysis of these products was possible. The dynamic mechanical properties of a typical segmented copolymer consisting of low molar mass segments is characterised by a single broad glass transition. This has been previously illustrated by the synthesised PBT - PDMS copolymer (Fig. 4.9) where one broad glass transition is observed at ~ - 30°C and the modulus varies gradually over a broad termperature range.

However, the products formed by catalysis using titanates show complex DMTA behaviour. Following reactions with no vacuum (Fig. 4.10), two distinct tan δ maxima are seen at ~ -80°C and ~ -62°C. These may possibly be assigned to two separate copolymer species which differ in siloxane composition. Following reactions where vacuum was used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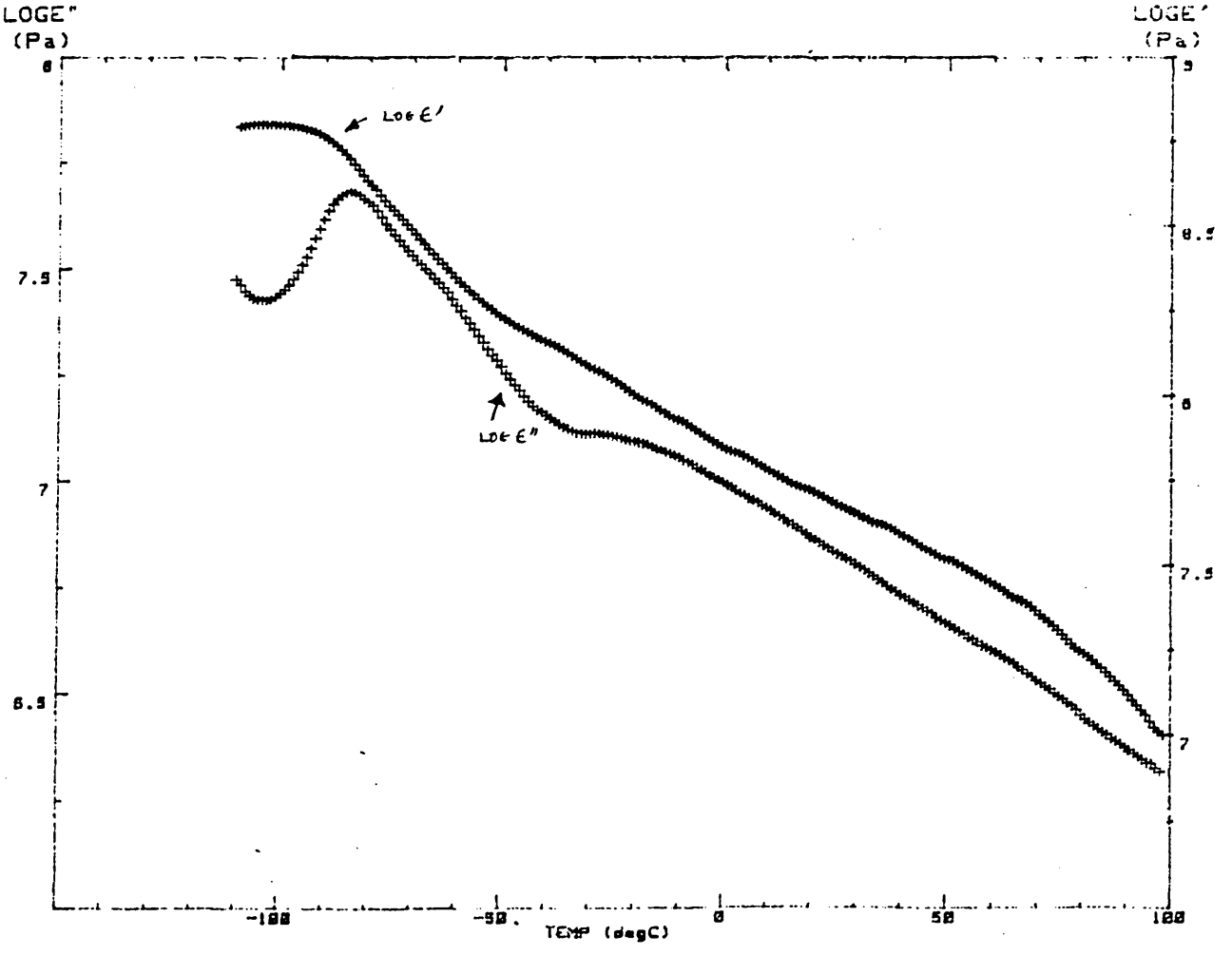
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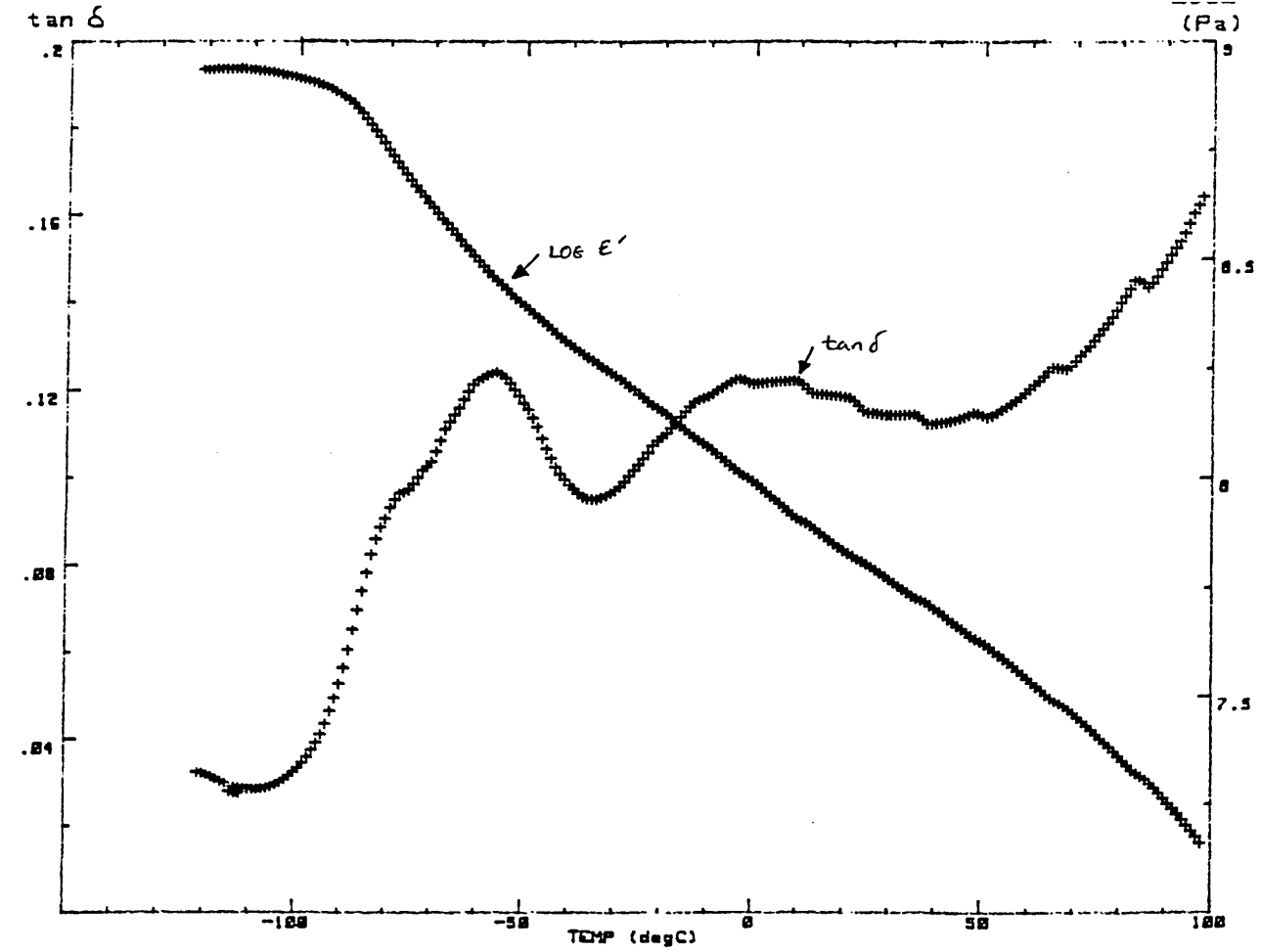
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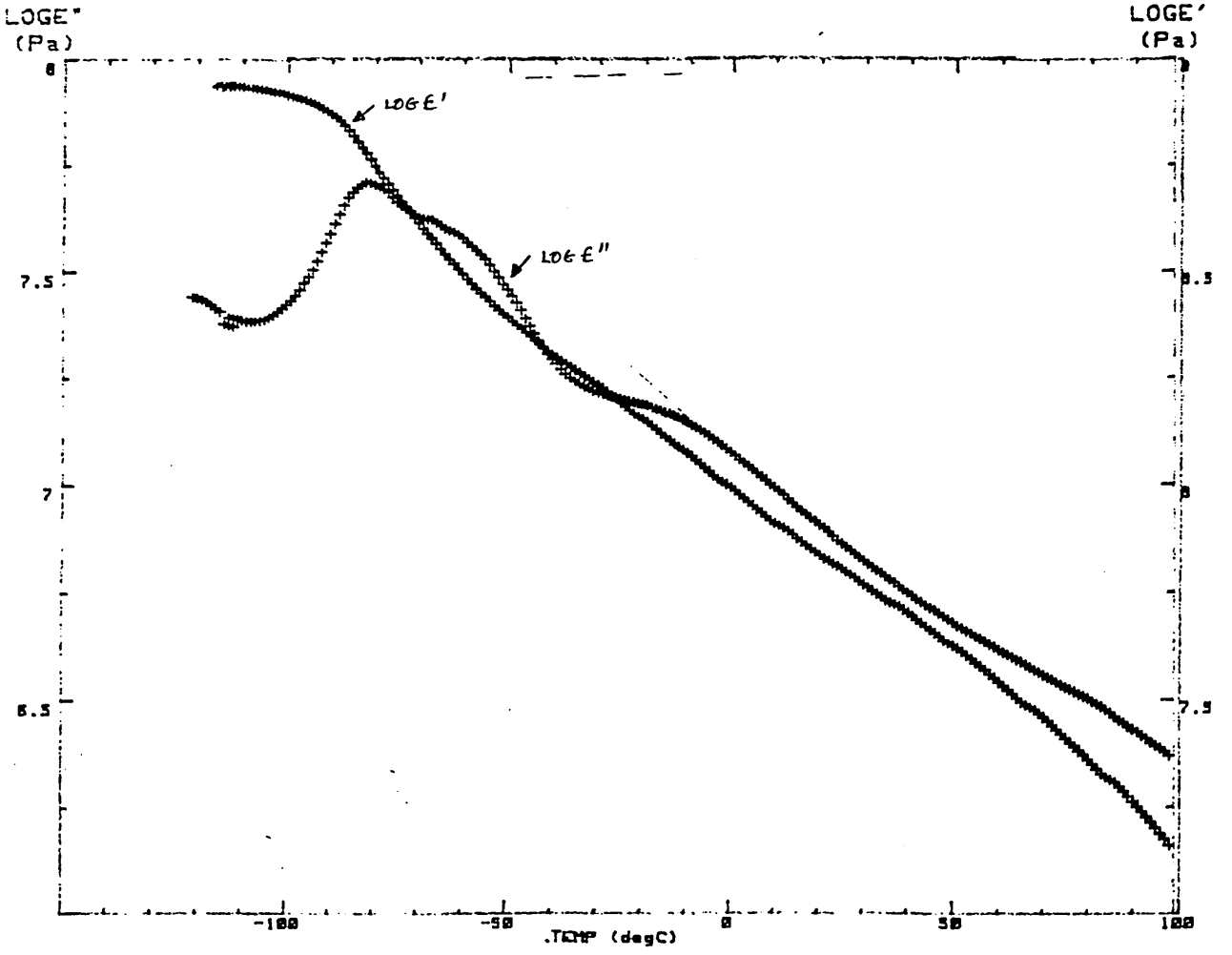
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(Fig. 4.11) there are again two distinct tan δ maxima but the maximum at ~-80°C is reduced in intensity. In both DMTA analyses there appears to be a possible additional tan δ maximum at ~ 10°C, being more prominent for samples prepared with no vacuum. This could be assigned to the Tg of the PBT segment. It is less pronounced in Fig. 4.11 since more PBT has been incorporated into the block copolymer. Unfortunately the siloxane Tg (-123°C) was not accessible by the instrument and therefore, it was not possible to assess the extent of any free siloxane present.

DSC analysis (Table 4.4) shows a decrease in the PBT melting point of approximately 20°C for the block copolymer samples, together with a significant decrease in the melting enthalpy which also becomes broad. This data indicates that limited block copolymer formation occurred.

Increasing the catalyst level from 1,000 ppm up to 12,000 ppm (with respect to PBT) failed to produce clear reaction mixtures or improve the mechanical properties.

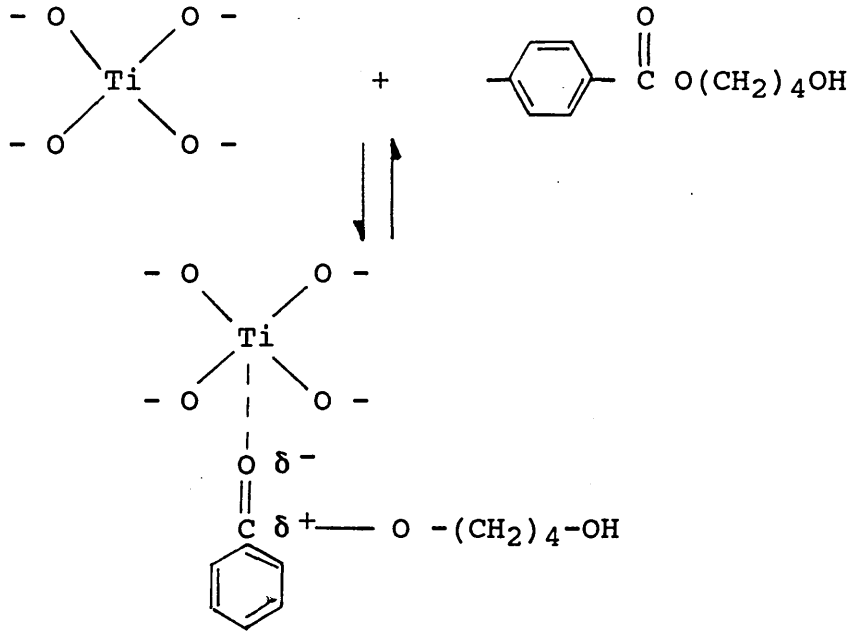
The failure of tetrabutyl and tetraisopropyltitanate to catalyse effectively the formation of a PBT - PDMS block copolymer is somewhat surprising as it has proved to be the most effective catalyst for PBT synthesis. It has also been effective in the preparation of polyether - polyester block copolymers (168) and in PBT/Ethylene vinyl acetate Blends (7).

TABLE 4.4 DSC Data for PBT - PDMS Block Copolymers (Titanate Catalysis)

Sample	MPt /°C	ΔH melt Jg^{-1}
PBT (A8 3102)	215.6	52.34
PBT/PDMS (50/50 m/m) (No vacuum applied)	195.8	21.89
PBT/PDMS (50/50 m/m) (Vacuum <1 mmHg for two hours applied)	193.4	15.97

N.B. ΔH_{melt} per g of copolymer.

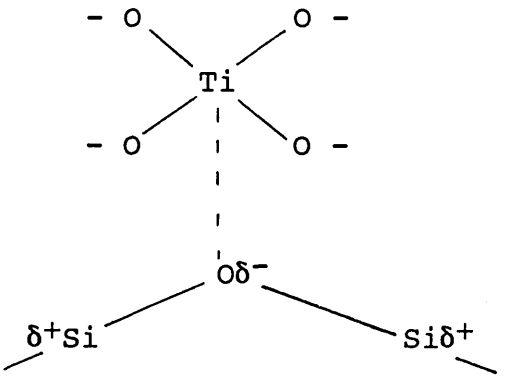
Pilati et al (208) suggested that the transesterification catalysed by tetrabutyltitanate is a co-ordinative mechanism involving the formation of an adduct between a carbonyl group and the Ti atom.



Reaction Scheme 4.9 Co-ordination Mechanism Of Ester Carbonyl Group To Titanium Species

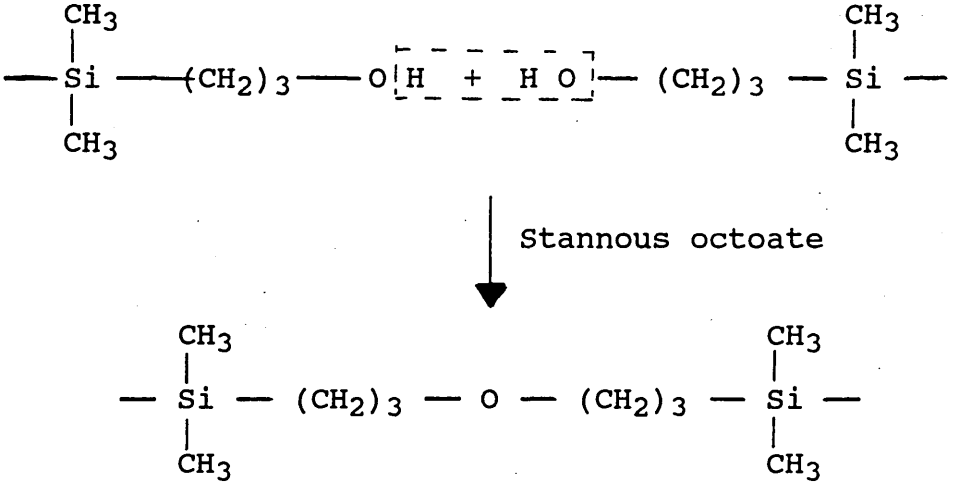
It is possible that a retarding of the siloxane may be due

to the formation of another adduct, between the siloxane backbone and the Ti atom. This may be more stable than the adduct between the carbonyl linkage of PBT and the Ti atom.



Reaction Scheme 4.10 Proposed Coordination of Siloxane Backbone to Titanium Species

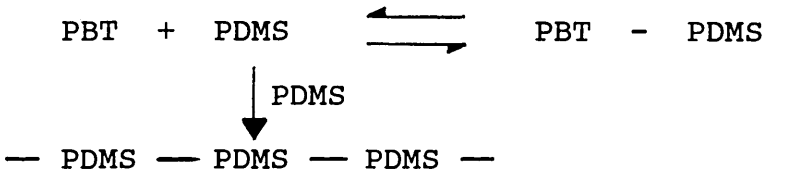
Stannous octoate proved to be successful in forming low RMM copolymers. However, stannous octoate is also capable of catalysing the condensation of α, ω hydroxy PDMS (209,210).



Reaction Scheme 4.11 Condensation of α, ω hydroxy PDMS.

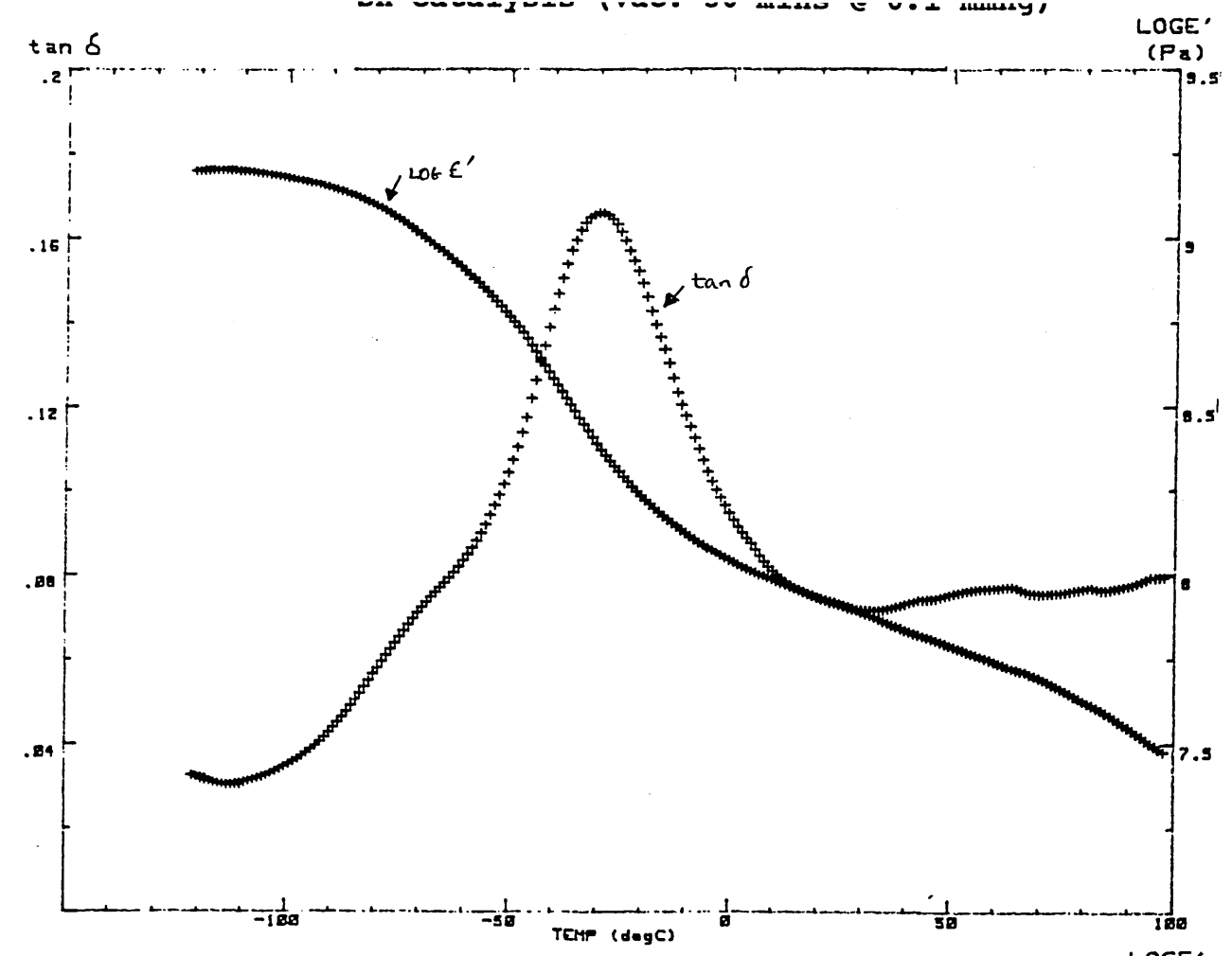
Copolymer formation by transesterification is an

equilibrium process, whereas the condensation of siloxane diols is not. Therefore, as the reaction proceeds the concentration of low RMM siloxanes available for copolymer formation is reduced since high RMM PDMS is formed by condensation.



Reaction Scheme 4.12 Competitive Reaction in PBT - PDMS Block Copolymer Synthesis

The extent of formation of high molar mass siloxane appears to be governed by the length of the reaction time especially when vacuum is used. DMTA analysis of the copolymer samples (Fig. 4.12, 4.13, 4.14) prepared with differing polycondensation periods show a broad peak which initially occurs at ~ -30°C but approaches -20°C as the polycondensation period increases. A further tan δ maximum at ~ -70°C becomes more significant for polymers prepared with longer polycondensation periods. Although in each analysis there is strong evidence for segmented copolymer formation, the appearance of two tan δ maxima which are beginning to approach the respective Tg's of the individual components, gives further indication of homopolymer formation.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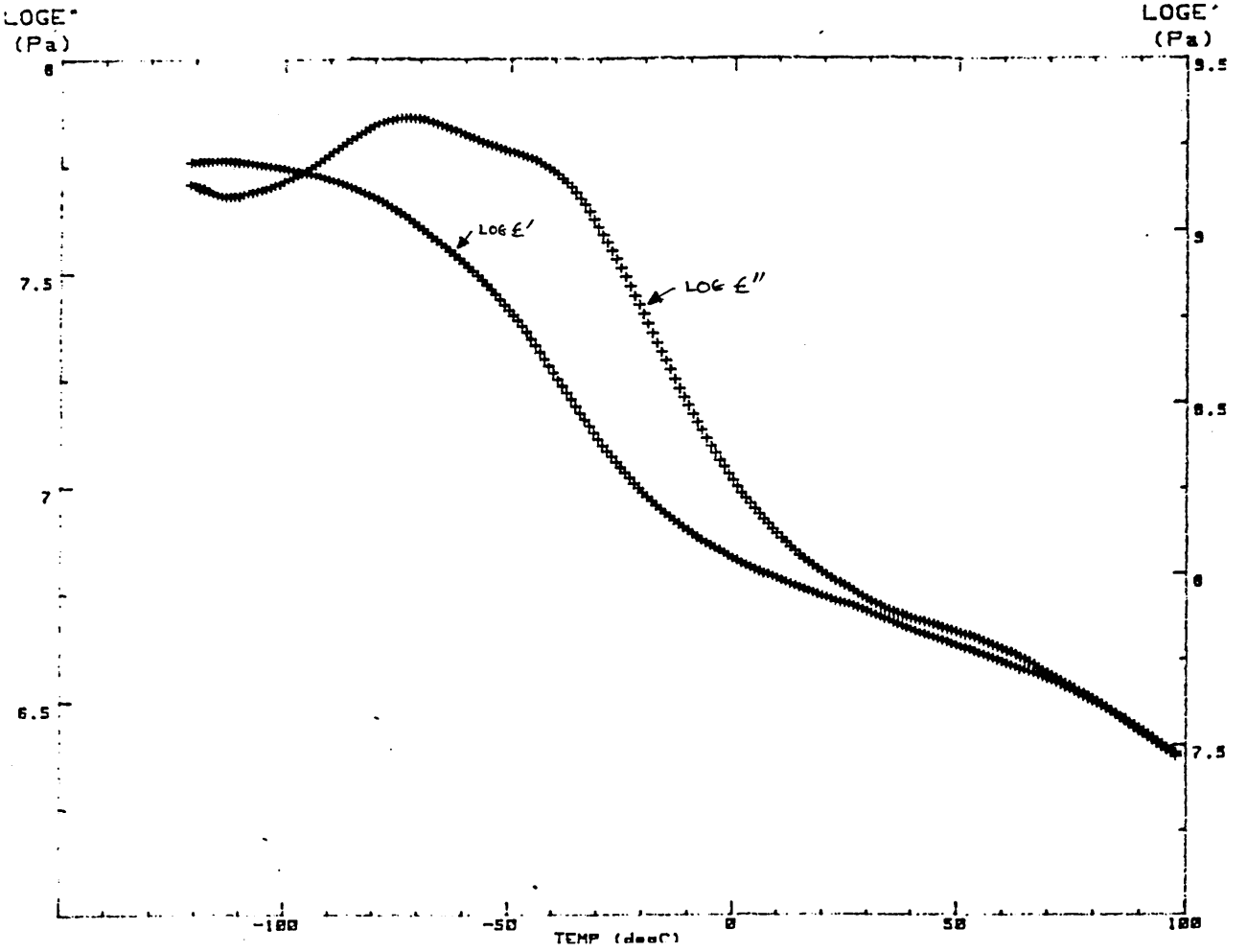
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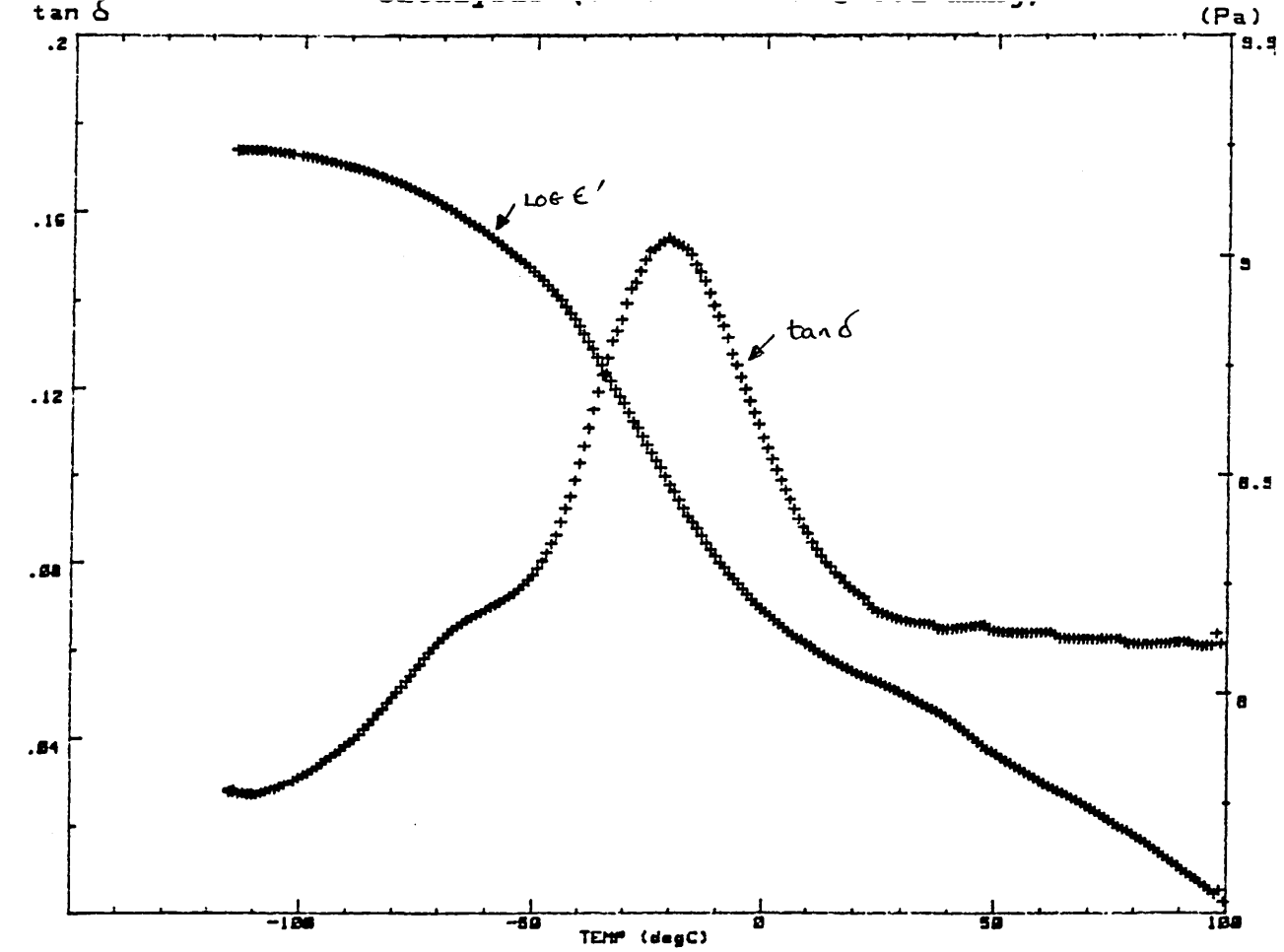
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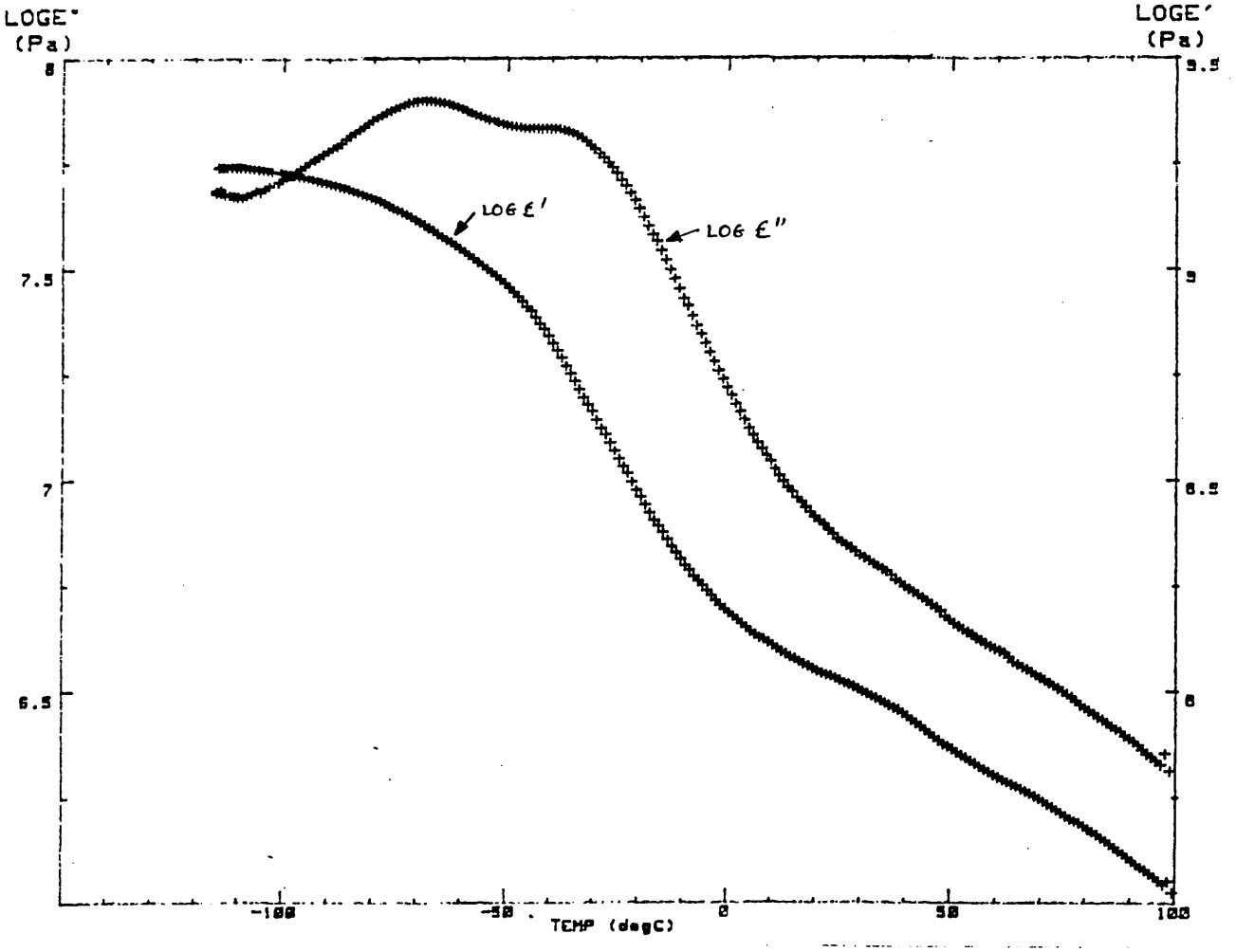
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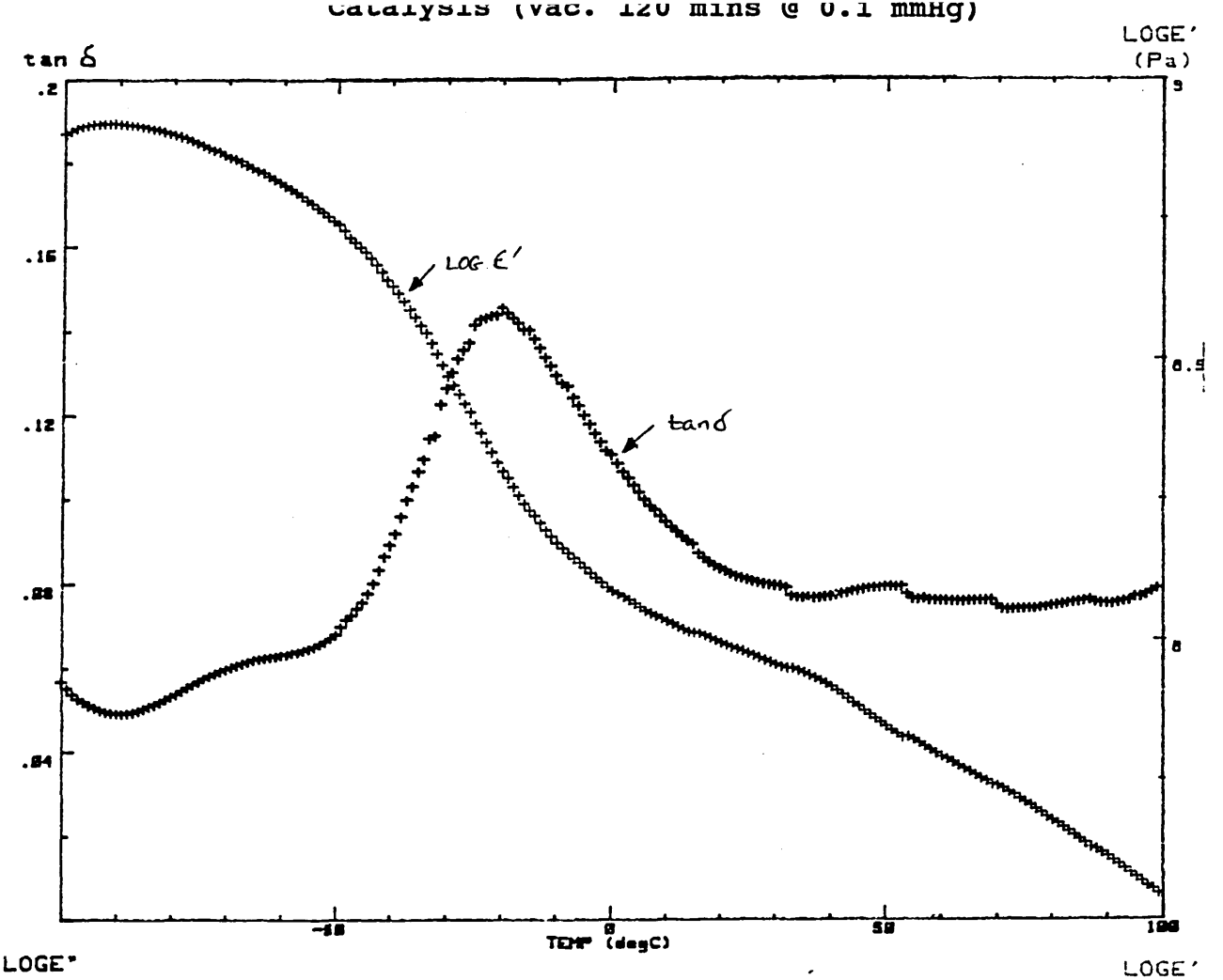
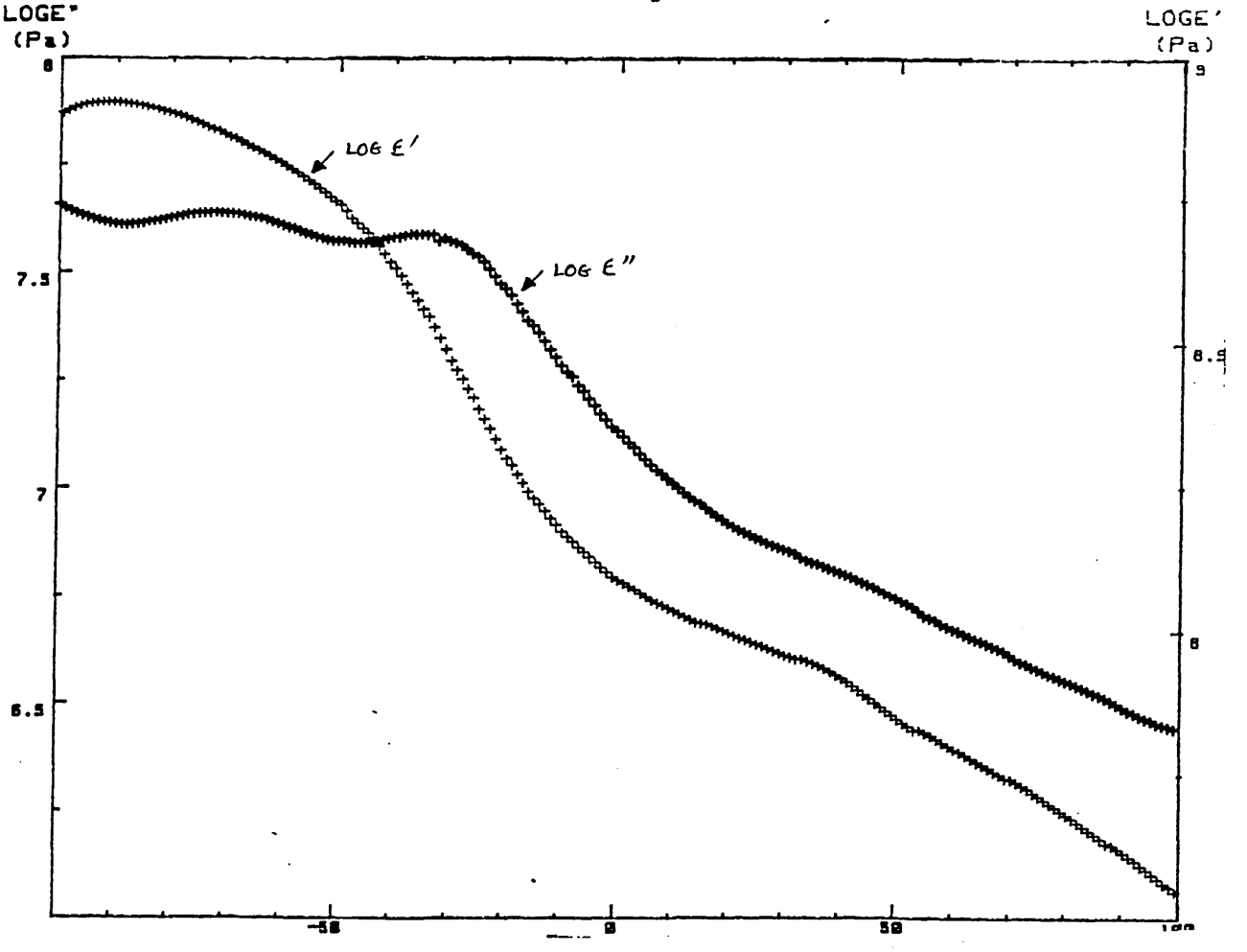
Catalysis (vac. 120 mins @ 0.1 mmHg)





DSC data presented in Table 4.5 show a reduction for the PBT melting endotherm peak of approximately 30°C. This indicates copolymer formation, and also shows that PBT segments all contain approximately the same number of repeat units in the chain (approximately eight), no matter how long the polycondensation period was. This was further confirmed by there being no significant change in the number average molar masses of the copolymer species (as measured by VPO) irrespective of the length of polycondensation period.

TABLE 4.5 DSC Data for PBT-PDMS Copolymers, Tin (II) Catalysis

Sample	MPt /°C	Δ H melt/Jg^{-1}	Mn
PBT (A8 3102)	215.6	52.34	2000
PBT/PDMS (50/50 m/m) Vac.10 mins @ 10 mmHg	184.3	27.64	2495
PBT/PDMS (50/50 m/m) Vac 30 mins. @ <1mm Hg	186.5	31.98	2363
PBT/PDMS (50/50 m/m) Vac 60 mins. @ <1mm Hg)	186.1	21.64	2580
PBT/PDMS (50/50 m/m) Vac 120 mins. @ <1mm Hg)	186.5	36.31	2574

Because of its ability to catalyse the siloxane condensation stannous octoate cannot be realistically used as a catalyst for the copolymerisation under discussion here. A number of potential transesterification catalysts

including dibutyl tin oxide and tetraisopropyltitanate were heated at 240°C with α, ω hydroxypropyl PDMS for two hours. Simple viscosity tests were used to indicate their effectiveness in catalysing the siloxane condensation. Dibutyl tin dilaurate and tin(IV) compounds which are said to be effective transesterification catalysts (211-214) appeared to be a possible candidate. The reaction mixture of PBT and PDMS with dibutyltindilaurate (DBTDL) as catalyst became translucent in the melt, and the product is homogeneous with elastomeric properties. DMTA analysis shows one broad transition (tan δ max (-30°C)) indicative of a segmented copolymer and DSC analysis shows a decrease in melting peak temperature and enthalpy of melting (Table 4.7). However, mechanical properties for the DBTDL catalysed copolymerisation show little improvement over stannous octoate catalysed copolymers, indicating the siloxane diol condensation could still be limiting high RMM block copolymer formation. Although with DBTDL this occurs to a slightly lesser extent.

Pilati et al (215) claim tin (IV) compounds to be poor transesterification catalysts for the synthesis of PBT. They increase the rate of reaction slightly over that found without catalyst, but the rate is two orders of magnitude lower than that using tetrabutyltitanate.

For the conventional ester interchange condensation, a number of acid and metal salt catalysts have been found to be active. Among the salts described are alkaline and alkaline earth oxides and hydroxides, antimony oxide, zinc acetate and transition metal acetates (216). Stackman (207) showed Ni (II) acetate to be one of the most effective catalysts for the preparation of aromatic polyesters by acid interchange polycondensation. However, when this was used here for the PBT - PDMS system, the product obtained was a soft white solid characteristic of an incompatible physical blend.

Since neither stannous octoate nor tetrabutyltitanate have proved to be successful catalysts for the formation of high RMM PBT -PDMS block copolymers, a combination of the two has been examined. Stannous octoate was initially employed to clear the system i.e. to form the low molar mass copolymer. Tris-(2,4-di-tert. butylphenyl)-phosphite (Irgafos 168) was then added to render the tin catalyst inactive and therefore, limit siloxane condensation. Titanium tetrabutoxide was then added for the polycondensation period. However, on addition of the titanium compound there was an obvious decrease in the viscosity of the reaction mixture. On applying vacuum a clear colourless liquid distilled over. This proved to be predominantly siloxanes. The product remaining was a soft white solid with very poor mechanical properties.

It would appear that the combination of stannous octoate, Irgafos 168, and titanium tetrabutoxide causes the depolymerisation of the copolymer liberating low molar mass siloxane oligomers. One possibility is that a strongly acid species is formed which redistributes the siloxane backbone. However, there is no chemical evidence to support this postulation.

Attempts were made to prepare copolymers from the monomers of PBT i.e. dimethylterephthalate and 1, 4 Butane diol and α,ω hydroxypropyl PDMS oligomers of low RMM ($\sim$ 1000g/mole). It was thought that commencing the reaction from the monomers of PBT would assist in reducing the incompatibility within the system. The initial mixtures of PBT monomers and siloxanes at 180^{o}C appear to be homogenous. However, the system very quickly became turbid and then white as methanol distilled over. The system became viscous at 180^{o}C, but the viscosity reduced once the higher temperature was reached. The final product obtained was a white solid of poor mechanical properties. In earlier experiments in which a lower stirrer speed was used phase separation of the two polymers occurred once PBT began to form. It would appear that it is preferable to use oligomeric PBT in copolymerisation reactions.

Another route to forming higher molar mass copolymers by transesterification is to utilise higher RMM oligomeric species. However, the effect of RMM on incompatibility of the two polymers is dramatically shown by increasing the

siloxane segment from 1,000 to 2,000, the higher oligomer being incompatible. A mixture of siloxane oligomers 1,000/2,000 (66.6% / 33.3% w/w) when reacted with PBT also proved to be incompatible.

However, altering the hard segment RMM does not have the same effect. The PBT oligomer was varied from 2,000 up to 6,000 RMM. The reaction was mixed for approximately an hour each time and then a short vacuum programmme (ten minutes at 5mm Hg) was applied to aid in the system becoming translucent.

DSC data of the products is given in Table 4.6. It was expected that increasing the hard segment molar mass would give a melting endotherm closer to that of pure PBT. However, surprisingly this was not so. The melting endotherms were obtained at ~ 185°C. Presumably an equilibrium is reached in the copolymerisation system in which the average RMM of the PBT segment is approximately the same, independent of the RMM of the initial PBT oligomer.

TABLE 4.6 DSC Data for PBT - PDMS Copolymers in which RMM of PBT Precursor has been Varied

Sample	M Pt /^{o}C	$\triangle$H melt Jg^{-1}
PBT (A8 3102) (RMM ~ 2,000)	215.6	52.34
PBT (RK123) (RMM ~ 2,700)	220.0	50.96
PBT (RK131) (RMM ~ 6,000)	222.8	49.26
A8 3102/PDMS (50/50 m/m)	184.3	27.64
RK 123 /PDMS (50/50 m/m)	180.4	22.57
RK 131 /PDMS (50/50 m/m)	186.7	29.42

Altering the mass composition of the two homopolymer components was investigated to establish whether reagent composition had any effect on the RMM of the final copolymer, as well as the melting temperature. Block copolymer synthesis earlier in this work is based on a composition of 50/50 m/m. A 67/33 m/m PBT/PDMS copolymer was attempted together with the converse ratio i.e. 33/67 m/m PBT/PDMS. Copolymers of each ratio were synthesised both with and without a significant polycondensation period with stannous octoate as the catalytic species. (The mechanical properties of these materials were assessed and the results are discussed in Chapter 5).

DMTA of the 67/33 ratio PBT/PDMS copolymer which has undergone polycondensation shows two distinct tan δ maxima at approximately - 65°C and 18°C (Fig.4.15). This indicates a small degree of phase separation due to the individual hard and soft segments. It would appear in this case the extent of transesterification of the PBT segment is not as great, resulting in a higher molar mass PBT segment in the copolymer. This is reflected in the DSC data (Table 4.7) and manifests itself in the increased incompatibility of the two individual segments in the copolymer. DMTA for the 33/67 copolymer which has undergone polycondensation (Fig. 4.16) is typical of a segmented copolymer with relatively small hard and soft segments i.e. one single broad glass transition with a tan δ maximum at approximately -30°C.

DSC analysis of the polymers (Table 4.7) gives further indication of copolymer formation with significant drops in the melting temperature from that of the PBT oligomer. Obviously there is a decrease in the temperature of the melting peak together with the enthalpy of melting as the mass/mass ratio of PBT to PDMS decreases.

Figure 4.15 DMTA Thermogram PBT-PDMS 67/33 Copolymer Sn Catalysis (Vac. 90 mins @ 0.1 mmHg)

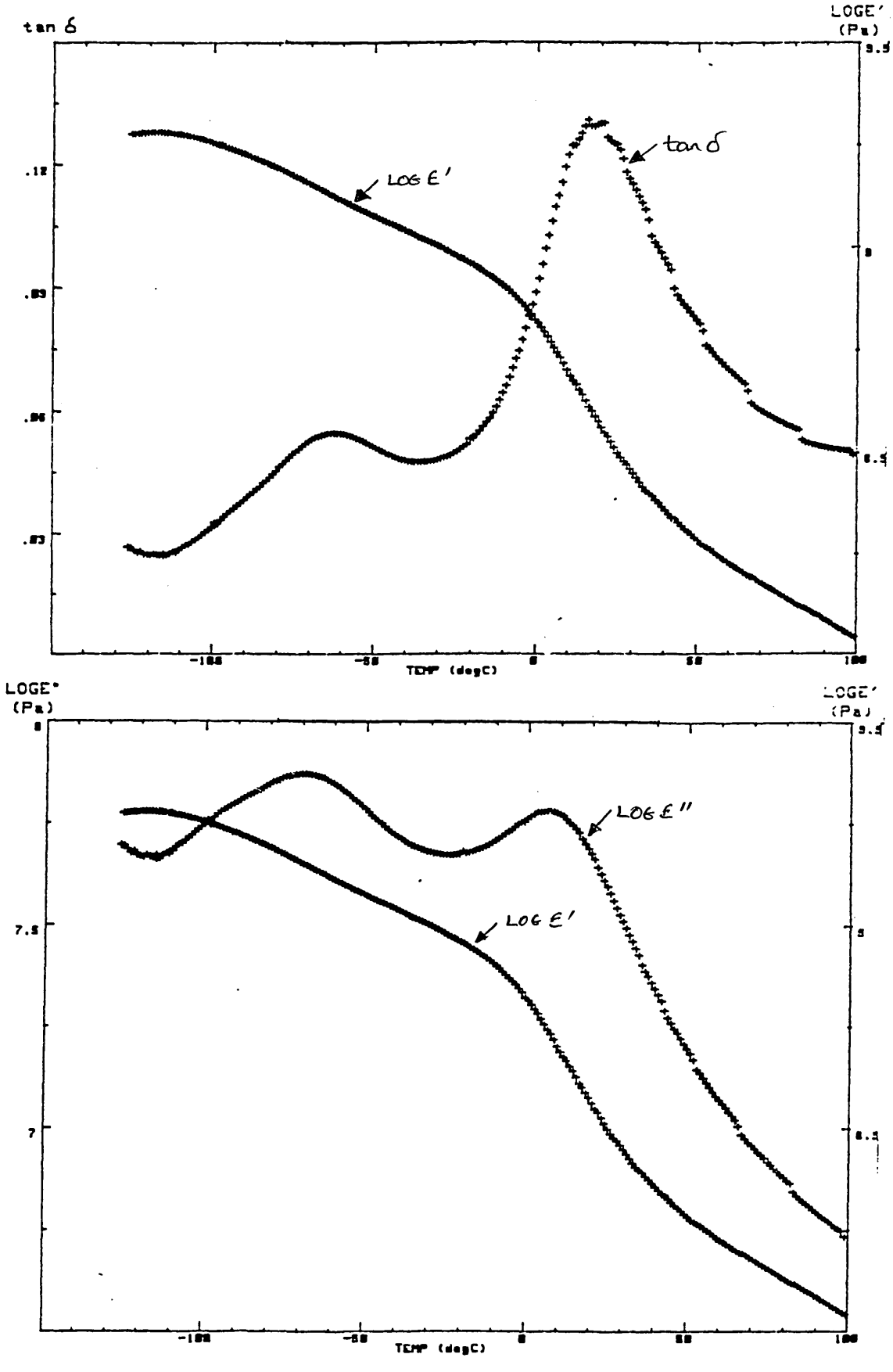


Figure 4.16 DMTA Thermogram PBT-PDMS 33/67 Copolymer

Sn Catalysis (Vac. 90 mins @ 0.1 mmHg)

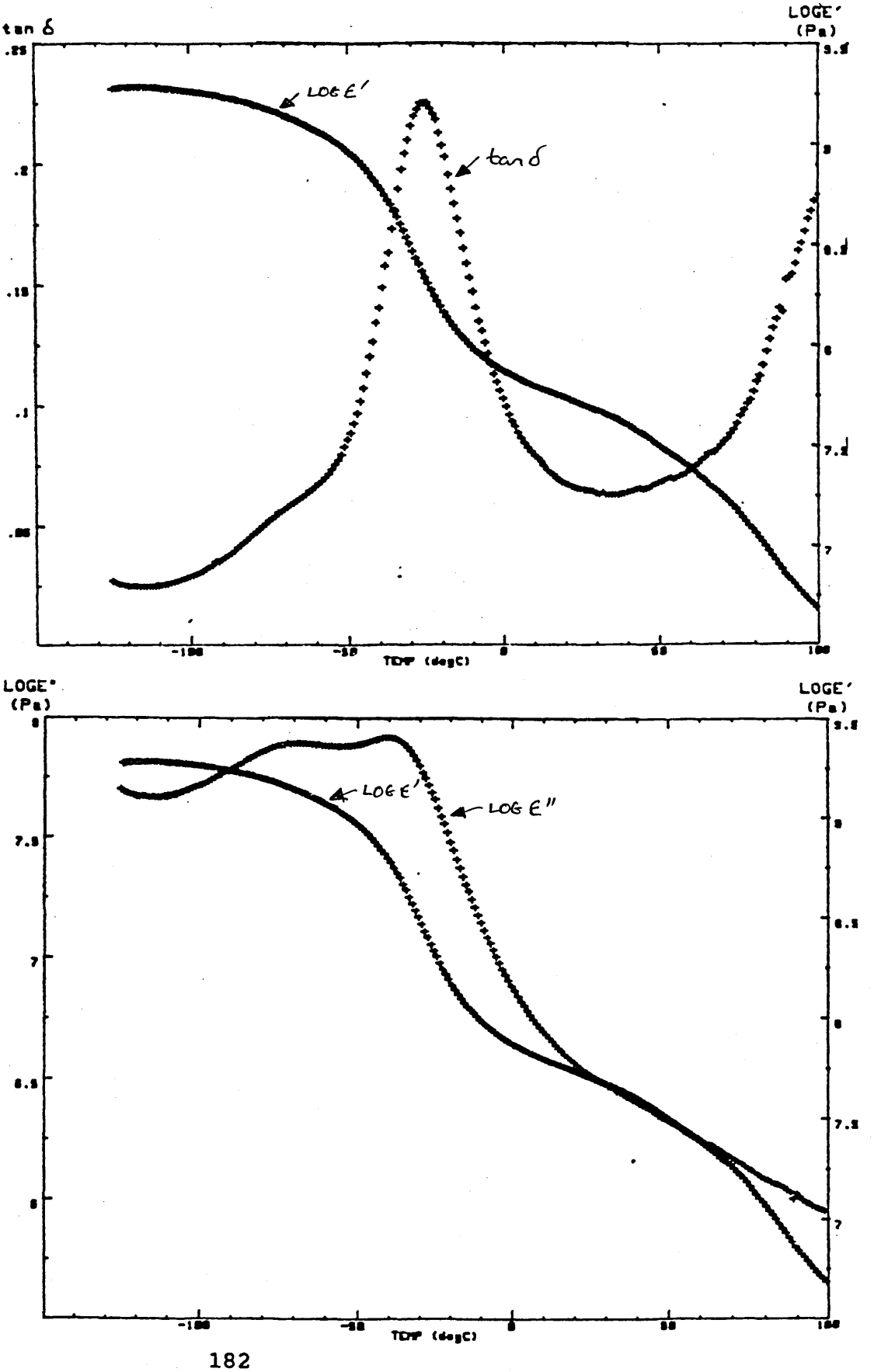


TABLE 4.7 DSC Data for PBT - PDMS Copolymers of Different Mass Composition

Sample	MPt /^{o}C	Δ H melt Jg^{-1}
1	204.6	39.95
2	205.1	40.89
3	161.0	19.61
4	198.1	20.77
5	196.2	19.06
6	193.2	32.44
7	184.3	27.64
8	186.5	36.31
9	215.6	52.34

Sample Index (Table 4.7)

1. PBT/PDMS (67/33 m/m) Stannous Octoate No Vacuum
2. PBT/PDMS (67/33 m/m) Stannous Octoate 90 mins Vac.
3. PBT/PDMS (33/67 m/m) Stannous Octoate 90 mins Vac.
4. PBT/PDMS (50/50 m/m) DBTDL No Vacuum.
5. PBT/PDMS (50/50 m/m) DBTDL 90 mins Vac.
6. PBT/PDMS (50/50 m/m) Plus MDI.
7. PBT/PDMS (50/50 m/m) Stannous Octoate No Vacuum.
8. PBT/PDMS (50/50 m/m) Stannous Octoate 120 mins Vac.
9. PBT (A8 3102).

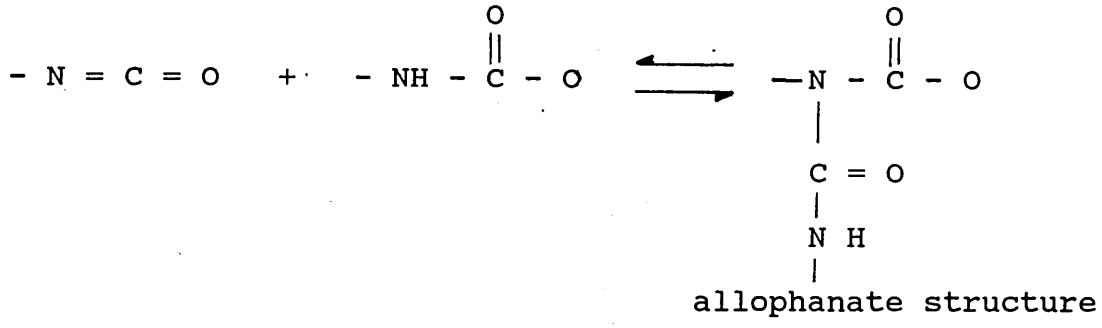
Copolymers are obviously formed at each of the chosen ratios and there is some improvement in the mechanical properties compared with the 50/50 m/m copolymer. However, the improvement is not great and the copolymers are still relatively weak and with relatively low RMM's.

4.324 Disocyanates as Coupling Agents for Low RMM Copolymer Precursors

The combination of ester interchange followed by polycondensation failed to produce a high RMM PBT - PDMS copolymer. However, by adding a difunctional diisocyanate to the cleared reaction mixture, it was intended this could increase RMM by acting as a chain extender.

A similar approach has been used by a number of companies in the preparation of segmented copolyester-ester elastomers (168). This route has been chosen since short reaction times are required (or deactivation of the catalyst usually a titanate) to reduce the extent of randomisation of the polyesters by transesterification.

The addition of the diisocyanate Diphenylmethane 4,4 Diisocyanate (MDI) to the cleared reaction mixture, causes a noticeable increase in viscosity. In order to obtain optimum mechanical properties the reaction was carried out using an excess of isocyanate to hydroxyl, preferably in the range 1.1 - 1.3. The use of an excess of diisocyanate leads to the formation of allophanate structures upon cooling the polymer melt to below 190^{o}C.



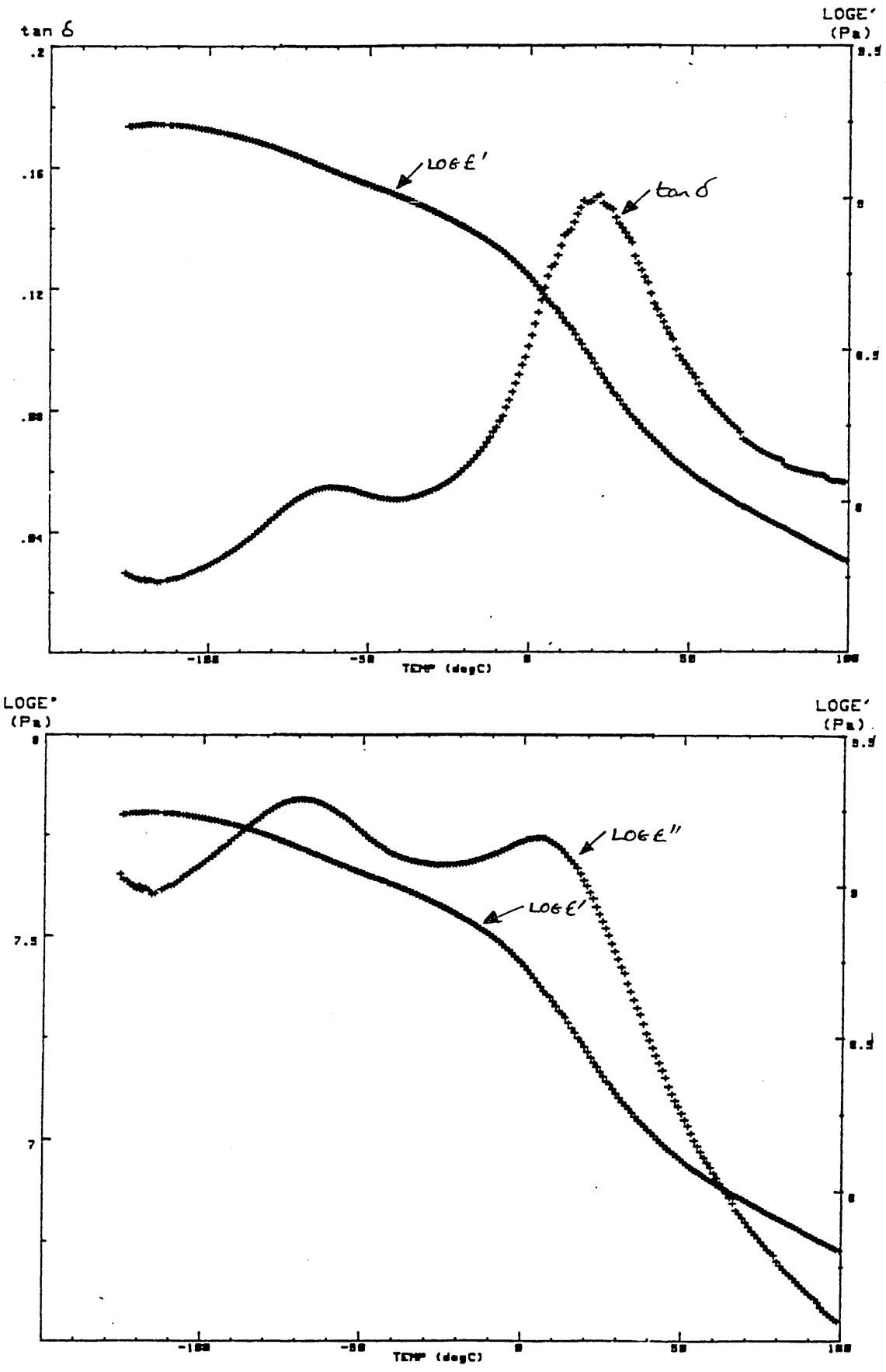
Reaction Scheme 4.13 Formation of Allophanate Structure

These allophanate crosslinks improve the mechanical properties and thermal processing remains possible since above 190°C the allophanate structures dissociate.

The DMTA trace of the copolymer (Fig. 4.17) shows two distinct tan δ maxima at 20°C and -65°C. This indicates a better degree of phase separation of the hard and soft segments. This observation is somewhat surprising since the allophanate crosslinks present in the diisocyanate extended copolymers would give rise to segments displaying reduced chain mobility. However, the increased RMM of the copolymer together with the siloxane being incompatible with both the urethane and the polyester segments probably contributes to the observed data.

Using the diisocyanate as an extender for low RMM PBT - PDMS copolymers has produced the copolymer with highest RMM so far, and consequently the one with the most promising mechanical properties (see Chapter 5).

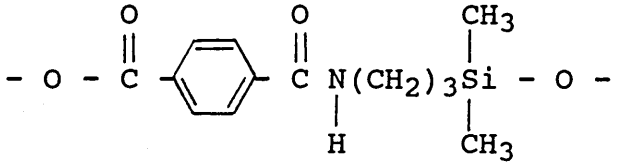
Figure 4.17 DMTA Thermogram PBT-PDMS Copolymer + MDI



4.325 Block Copolymer Formation by Amidation

Transesterification has proved to be a viable route to forming low molar mass PBT - PDMS copolymers. However, hydroxy siloxane condensation together with the lack of a specific suitable catalyst have restricted this approach.

On reacting an amine terminated PDMS with PBT under melt conditions, it was hoped a transamidation reaction would occur.



The amine group is expected to be more nucleophilic to the carboxyl linkages along the PBT backbone, than hydroxyl groups. General Electric Company have claimed a similar procedure (184) for forming siloxane polyester copolymers. A further benefit of using amine terminated siloxanes is that there is little chance of self condensation.

Initial experiments concentrated on α, ω aminopropyl siloxanes of approximate RMM 1700. Unfortunately this material proved to be too incompatible with PBT the reaction mixture phase separating on removing vigorous agitation.

Further experiments used aminopropyl siloxanes of RMM 1,000 together with imidazole as catalyst. Imidazole was used as catalyst due to its high boiling point. The reactions were carried out at temperatures of 240°, 260° and 280°C respectively. Each experiment however, failed to give clear mixtures and the reaction products were brittle white solids.

A possible reason for the failure of the copolymer formation using the aminopropyl siloxane was that it is less compatible with PBT than its hydroxy siloxane equivalent. The - OH groups aid the affinity of the siloxane to the polyester. Owing to the incompatibility problem no further investigations were carried out.

4.326 Reaction of Polyethylene Glycol Capped PDMS with PBT

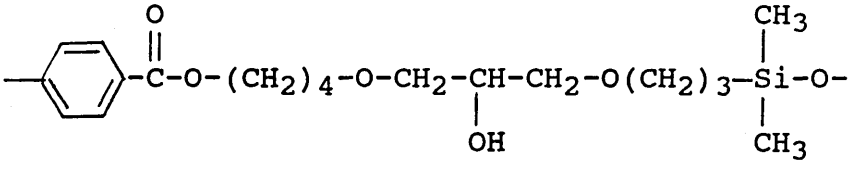
The purpose of attaching low molar mass polyethylene glycol (PEG) oligomers was two-fold. Firstly, polyethylene glycol oligomers have been shown to react successfully with PBT to form copolymers (168). Therefore PEG terminated PDMS may also react, the PEG oligomers being present to aid the affinity of PDMS towards the PBT. Secondly, using the PEG functionalised siloxane should prevent siloxane self condensation occurring during copolymer formation.

However, in practice it was found that the product was a soft white solid characteristic of an immiscible blend. It appears that the increase in RMM of the soft segment by addition of the PEG groups, rather than improving the affinity of the siloxane segment towards PBT,actually decreases it. This is probably not so surprising due to the narrow range that is apparent between RMM of siloxanes which are compatible with PBT. For example the observed compatability difference between 1,000 and 2,000 RMM siloxanes and oligomeric PBT.

Owing to the apparent increased incompatibility of the siloxane segments further reactions were not attempted.

4.327 Reaction of α,ω diepoxy PDMS with PBT

α,ω diepoxy PDMS oligomers were successfully synthesised in the laboratory. However, they were not used for copolymerisation reactions, since the reaction between α, ω hydroxy PBT and epoxy siloxanes would give a secondary hydroxyl group on the ring opening of the oxirane ring.



The secondary hydroxyl groups are then available for further reaction with epoxy siloxanes, possibly leading to epoxy siloxane polymerisation. Transesterification reactions could also occur along the PBT backbone, reducing the oligomer RMM significantly. Because of these distinct side reaction possibilities, this copolymerisation route was not pursued.

5.1 Introduction

The enhancement of toughness in thermoplastics is widely achieved commercially by blending with flexible additives such as elastomers. This approach has previously been employed with some success in, for example, the production of high impact polystyrene (HIPS) a blend of polystyrene with a suitable rubber, usually polybutadiene and rubber toughened PVC (217).

Rubber toughening in polymer blends is dependent on the separation of the two components into a stable two phase system. The rubber must be dispersed randomly as small discrete particles in the continuous matrix phase if significant improvements in impact toughness and fracture behaviour are to be achieved. For this phase separation to occur the components must display a certain minimum degree of thermodynamic incompatability. That is, they must have a positive free energy of mixing and therefore be immiscible. Other factors necessary for efficient rubber toughening in such a two phase system include good adhesion of the rubber particles to the matrix and an adequate dispersion of rubber particles of dimensions close to the optimum for each particular matrix material.

A variety of quite different theories have been proposed to explain the mechanism of rubber toughening in phase separated polymer blends, the most common being attributed to crazing and shear yielding, although absorption of energy by rubber particles and yielding of the continuous matrix have been proposed too. These may be briefly summarised as follows:

1) Absorption of energy by the occluded rubber particles. This theory was first proposed by Merz et al (18) based on data from studies on a styrene-butadiene rubber/polystryene matrix system. It was suggested that the rubber particles held together the fracture surface of a developing crack undergoing extensive elongation as the matrix material parted, and absorbed more energy than the equivalent volume of the continuous phase.

2) Absorption of energy by yielding of the continuous matrix immediately adjacent to the rubber particle.

This explanation was proposed when it was determined that energy absorbed by the rubber accounted for only 10% of the total energy absorbed in certain composites. Low volume change of the rubber particle on deformation (due to its Poisson ratio of about 0.5) was thought to lead to increased yielding of the matrix locally, and hence increased energy absorption, in order to maintain the volume expansion of the strained material.

3) Multiple craze formation initiated by rubber particles.

Formation of crazes (regions of plastically deformed porous material which scatter light due to their low refractive index) occurs near the rubber - matrix interface. The rubber particles serve as local concentrations of stress and thus lower the critical stress necessary for craze initiation in the blend. A large amount of energy is absorbed during craze formation (associated with the local orientation that occurs in the craze) and therefore deformation of the material when subjected to stress is effectively limited. In addition, the rubber particles act as craze termination points. These delay the development of crazes into a crack of a critical length beyond which the material would be subject to catastrophic failure.

4) Shear yielding as a source of energy absorption and crack termination.

It has been proposed that shear yielding in the matrix phase may play some role in the mechanism of rubber toughening in polymer blends. Shear yielding, as localised shear bands or more generalised and diffuse regions of shear yielding, usually occurs in addition to elastic deformation. This phenomenon not only acts as an energy absorbing process but the shear bands also present a barrier to the propagation of crazes and hence crack growth (1), therefore delaying failure of the material. The stress concentrations produced by rubber particles at the rubber matrix interface are known to be initiation sites,

for the shear bands as well as crazes.

It is now generally accepted that the energy absorption in the rubber toughening mechanism operative in polymer blends occurs principally in the polymer comprising the continuous matrix phase. The major role of the rubber particles seems to be the control of the deformation processes associated with this. This control is exercised by the provision of a large number of stress concentrations where localised deformation is initiated and sites where crazes are terminated. A particular toughened thermoplastic system may therefore, fail principally by multiple craze formation or principally by shear yielding or, as is often the case, both failure mechanisms may be exhibited by the system to some extent.

5.11 Structure - Property Relatioinships

Many workers (30-32,218,219) have correlated the concentration and size of the dispersed particles in multiphase polymers to their fracture behaviour. The size of the included rubbery particles has a great influence on the efficiency of impact modification and there is a minimum particle size below which no significant toughening occurs (220).

Some consensus has been reached that an optimum particle size of the rubber (29,30) exists and depends on the mechanism of fracture. Where failure occurs through craze formation, the optimum particle size is higher than when a shear yielding mechanism is operative. Some studies have also been carried out on the influence of crosslinking of and grafting to the rubber. The conclusions concerning the effect of rubber crosslinking are rather ambiguous (221,222) but a small extent of crosslinking should give optimum properties (1,221-223).

Attempts to understand the role of the rubber particles and why an optimum size exists have focussed primarily on their ability to initiate crazes and/or shear bands (1,25,26,28). For example, polystyrene fractures by a crazing mechanism; formation of microvoids precedes the actual development of cracks (18,24). Hence the role of the rubber inclusions is both to initiate and to terminate such crazes. These effects are accomplished most efficiently when the size of the rubber particles is in the range 2 to 4 μm (18,29,30).

A polymer like PVC, which is more ductile than polystyrene, fails by shear yielding. The optimum particle size for impact resistance should should be in the range of 0.1 to 0.2 μm (1,30). These results show that the critical particle size for toughening decreases with increasing ductility of the matrix polymer.

One explanation of this phenomenon is that in relatively ductile polymers craze growth is inhibited by shear

yielding, the rubber particles being too small to control crazing directly, but large enough to control it indirectly by initiating shear bands.

Correlations between rubber concentration and toughness have been reported for many rubber modified polymers including those based upon polystyrene (218,219,224), epoxy resins (20,225,226) and nylon (31,32). However, in many of these only the concentration of the rubber added initially was known. This may of course, be considerably different from the actual rubber phase volume fraction present after polymerisation. A further complication in correlating concentration of rubber particles to fracture behaviour is that microstructural features such as rubber volume fraction, particle size, particle size distribution and internal particle structure are all often interrelated so it is difficult to change progressively one feature independently of the others.

Some studies have addressed these problems in toughened polystyrene (227); impact strength passed through a maximum at a rubbery phase volume fraction, of about 0.2. This maximum may be explained from the observation that the average particle size increased with increasing rubber phase volume. In epoxy resin studies (225,228) increasing rubber phase volume caused a concurrent increase in the fracture energy up to a maximum of about 20% w/w. This maximum occurs because at higher concentrations the rubber does not form a separate particulate phase, but instead a

single phase blend is produced.

5.12 Particle-Matrix Adhesion

The rubber-matrix adhesion is critical in impact modification of plastics. The rubbery particles must be adequately bonded to the matrix to be effective as sites for controlled craze or shear-band growth, to prevent premature craze breakdown and crack initiation, or even to act as simple energy absorbers via deformation and fracture behind the crack front.

Early toughened thermoplastic materials prepared by melt blending rubber and thermoplastic together yielded multiphase polymers in which the rubber particles were only poorly bonded to the surrounding matrix. The result was a far less tough material than expected. In addition, a poorly bound rubber particle can be deformed readily during processing, forming a lamellar structure, which delaminates on injection moulding and impact testing.

Much tougher systems are obtained by increasing the stability of the particles by chemical grafting the rubber particles. HIPS, ABS and toughened PMMA are prepared by techniques which lead to grafting reactions. In these materials such reactions are typically induced by first preparing a rubber latex by emulsion polymerisation. Monomers are then added to the reactor vessel and polymerised in the presence of the rubber latex (1).

Some materials, e.g. PBT, PVC, do not readily adapt to this type of graft polymerisation technique, so it is necessary to blend the rubber into the matrix polymer as a separate process. As previously mentioned, under such circumstances, the rubber should possess a solubility parameter sufficiently different from the matrix polymer to ensure a fine second phase dispersion, but close enough to promote adequate adhesion of the particle to the matrix (229). Obviously this limits the choice of rubber.

Block copolymer technology has offered a new range of blended multiphase polymers where good particle/matrix adhesion is relatively readily obtained without compromising mechanical properties. Essentially, a suitable block copolymer is added so that it acts as an interphase region between the particle and the matrix. Segments of the block copolymer are located in both particle and matrix and this provides good adhesion without the need to reject a desirable elastomer candidate because of its solubility properties. In fact copolymer techniques have produced toughened polystyrene (230) possessing extremely high impact strengths that are usually superior to normal grafted HIPS material.

5.13 Basic Thermodynamic Considerations in Polymer - Polymer Miscibility

Chemically different high molar mass polymers are normally incompatible and their blends, when cooled from the melt or cast from solution, undergo macroscopic phase separation with complete segregation of the components at equilibrium (231).

In a small number of cases the simple blending of a thermoplastic and rubber additive results in the formation of a compatible single phase blend. Generally, however the formation of a two phase system of rubbery particles in a rigid matrix is observed.

The formation of a two phase system is crucial to the rubber toughening of polymers and some insight into which systems are likely to display this phenomenon is required.

The state of miscibility of any mixture is governed by the free energy of mixing ΔG_{mix}, given by:

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad \text{Equation (5.1)}$$

where ΔH_{mix} is the enthalpy change on mixing and ΔS_{mix} is the entropy change on mixing. Miscible mixtures will occur whenever the free energy of mixing is negative.

It is useful to employ thermodynamic models that permit some estimates of the terms in equation (5.1). The simplest model for polymer - polymer mixtures is the Flory-Huggins theory, which when applied by Scott(232) to polymer blends, gave the following expression for the enthalpy and entropy of mixing.

$$\Delta H_{mix} = B V \phi_1 \phi_2 \quad (5.2)$$

$$\Delta S_{mix} = -\frac{R V}{V_r}\left[\frac{\phi_1 \ln \phi_1}{X_1} + \frac{\phi_2 \ln \phi_2}{X_2}\right] \quad (5.3)$$

where V_r is a reference volume,

V is the volume of the mixture,

B is the mixing energy density characteristic of polymer - polymer segmental interactions in the blend,

X_1 is the degree of polymerisation of component 1,

ϕ_1 the volume fraction of component 1

R is the gas constant.

The entropy of mixing two polymers is dramatically less than that for two low molar mass species. Equation (5.3) shows that ΔS_{mix} is a function of molecular size and tends towards zero with increasing molar mass.

The enthalpy of mixing, on the other hand, is primarily dependent on the energy change associated with nearest neighbour contacts during mixing (233) and is virtually independent of molecular lengths. The net result is that ΔG_{mix}, is primarily influenced by the sign and magnitude of ΔH_{mix} for high RMM mixtures. For weakly interacting

materials (i.e. only dispersive or Van der Waals type bonding between segments) the heat of mixing is estimated from the difference between the solubility parameters δ_i of the pure components (233) by the equation

$$\Delta H_{mix} = V (\delta_1 - \delta_2)^2 \qquad (5.4)$$

Equation (5.4) always predicts a positive enthalpy of mixing or at best zero when δ_1 is exactly equal to δ_2. Thus miscibility in such cases is predicted to be a highly unlikely event in systems for which equation (5.4) offers an adequate prediction. This relation shows the need of structually similar components in order to find miscibility. As well as predicting miscibility the converse is true and the relationship between $(\delta_1 - \delta_2)^2$ and ΔH_{mix} has been used to predict whether a specific rubber would be a good toughening additive for a specific brittle polymer.

As previously stated two necessary requirements for good rubber toughening are the formation of two phases and good adhesion between phases. Stehling et al (13) attempted to place these two requirements on a more quantative basis. They observed that phase separation would only occur if the absolute value $(\delta_1 - \delta_2)$ is sufficiently large. Following Krause (234), and assuming a molar mass of 10^5 for each component, they calculated that the critical value of the solubility parameter difference $(\delta_1 - \delta_2)_{cr}$, which must be exceeded for phase separation to occur, is 0.4 $(MJm^{-3})^{1/2}$

for rubber contents of 5-10% at 25°C.

Adhesion between polymer pairs was considered with the aid of Helfand's theory for the thickness of the interface between two polymer phases (235). This theory states that the interfacial thickness increases as $(\delta_1 - \delta_2)$ decreases.

Stehling introduced the hypothesis that good adhesion requires physical entaglement between the two kinds of molecules in the interface. Taking the number of chain bonds between entanglement points (236) to be typically 500, a bond distance of 0.15 nm, and assuming freely jointed, they calculated the root-mean-square distance between entanglements to be $0.15 \times 500^{0.5}$nm i.e. 3.3nm. This leads to the conclusion that the interfacial thickness should be greater than 3nm for good adhesion. This requires that $(\delta_1 - \delta_2) < \sim 0.8$.

Thermodynamics does not limit us to systems which mix endothermically; if the heat of mixing is exothermic then the above mentioned restrictions to polymer - polymer miscibilty no longer apply. This is because the negative contributions to the free energy of mixing are not restricted to the rather small contribution to be expected from a positive combinatorial entropy of mixing.
As enthalpic interactions result from short range forces between adjacent centres, a reasonable test of the necessity of exothermic interactions for the formation of

miscible blends would be to compare the observed miscibilty of polymer pairs with the calorimetrically observed heats of mixing of their low molar mass analogues. Work with blends of polycarbonate and polyesters (237) confirmed this theory.

However, predetermining the potential for miscibility from knowledge of the chemical structure of a given polymer pair remains unresolved. Gutmann (238) indicated for example that molecules which behave as Lewis bases in a particular molecular environment may behave as Lewis acids in another. The result of this behaviour is that the interaction between different species is a function of their relative acid or base-like behaviour. However, it appears from experimental information gathered that some degree of exothermic interaction between the binary polymer components is necessary for miscibility. Dispersive interactions between weakly interacting non polar materials leads to positive heats of mixing and polymer pair immiscibility e.g. HDPE and LDPE (239), despite the similarity of their chemical structures. Miscible polymer pairs have chemical structures capable of interacting by a variety of specific mechanisms which include hydrogen bonding, complex formation, phenyl group coupling and dipolar interactions. The number of different specific interactions leading to miscibility is encouraging from the point of discovering new miscible blends.

5.14 Phase Separation in Block Copolymers

As previously noted, the blending of two polymers usually results in macrophase separation. In block copolymers, however, incompatible polymers are linked to each other via a covalent bond. This bond inhibits macroscopic phase separation, and instead these systems often exhibit separation on a micro scale (11,12). The presence of covalent bonds in copolymers places some constraint on the number of possible arrangements, resulting in an appreciable loss in configurational entropy of mixing. Because of the entropy loss, the critical molar mass required for microphase separation in copolymers is predicted to be considerably higher than in analogous homopolymer mixtures. Experimental observations support these theoretical predictions (240).

The available theories of the phase separation phenomena are quite rigorous, but they are inadequate, as they rely on Flory's interaction parameter, λ_{AB} (241), which is at best a rough approximation (poorly defined for polymer - polymer interactions) and is somewhat limited to non-polar polymer systems where only dispersive interactions are important. It will invariably be erroneous when specific interactions exist.

Meier (14,16,240), on studying A - B and A - B - A copolymers established the thermodynamic criteria for phase separation and determined three contributions are required to account for the entropy difference between the block

copolymer and that of a simple mixture of the components. They are,

a) The restriction of the position of the A - B covalent bonds between the domains results in an entropy decrease termed the "placement entropy" ΔS_p.

b) A further reduction in entropy, due to the requirement that A segments remain in domain space of A and that B segments remain in B domain arises and it is termed the "restricted volume " entropy difference ΔS_v.

c) The third entropy difference (also a decrease relative to the simple mixture) arises from pertubation of chain dimensions in the domain system from the random flight values. This is termed the "elasticity entropy" ΔS_{el}. The equilibrium domain size and shape are a result of the balance of these three free energy terms.

The minimum molar masses required for domain formation for the AB_- block copolymer versus phase separation of simple polymer mixtures were computed by Meier. Using appropriate estimations, he determined that phase separation in a block copolymer requires a significantly higher molar mass than in one of analogous homopolymer mixtures.

Further work by Meier (242) allowed a quantitative estimate of the size of the interfacial zone between segments of A and B, in an A - B diblock copolymer, to be calculated as a fraction of the system volume. To a first approximation this was estimated to be a function only of the product of the copolymer molar mass (m) and a measure of the segmental interactions estimated by the solubility parameter difference for the two segment types ($\delta_A - \delta_B$).

When the volume of the interfacial zone between A and B segments of the copolymer is near zero a sharp interface exists. This requires a high molar mass or a large segmental interaction such that the function $m (\delta_A - \delta_B)^2$ is very large. If the interfacial volume fraction is near unity there will be no segregation into domains. This occurs at very low molar mass or with very small segmental interactions e.g. $\delta_A \simeq \delta_B$.

Leary and Williams (243,244) were the first to realise that the interphase between dissimilar segments was diffuse and had a finite thickness. A major difference between their treatment and Meier's is their incorporation of a mixed region at the interface which is assumed to exhibit single-phase behaviour. The entropy of phase separation was considered to arise from three contributions;

$$\Delta S_{tot} = \Delta S_1 + \Delta S_A + \Delta S_B \qquad \text{(Eqn. 5.5)}$$

ΔS_1 is the entropy change resulting from the requirement that one of the junctions of the A - B blocks must be placed in the mixed region. ΔS_A is due to the requirement

that A blocks remain in A domains or the mixed region, and ΔS_B results from locating the B blocks outside the A domain with both ends of the block in the mixed region. The model actually predicts the specific microstructure which is thermodynamically favoured.

A different approach concerned only with thermodynamic phase separation and not with the morphology of the domain structure, was developed by Krause (245 - 247). This treatment is not limited to a particular type of block copolymer (e.g. A - B); it is applicable to $(AB)_n$ systems as well as to mixtures of one or more of the copolymers with the constituent homopolymers. Krause assumed the following in the development of her method;

(1) The block copolymers are monodisperse.
(2) The same number of blocks and sequence distribution exists within each molecule.
(3) Complete separation exists between the constituent phases
(4) Any homopolymer present is monodisperse and is miscible only with its analogous phase.
(5) The lattice model is applicable .

This model predicts that phase separation becomes progressively more difficult as the number of blocks increases in a copolymer molecule of given length. It predicts easier phase separation when the molar mass of the block copolymer increases at fixed copolymer composition and number of blocks per molecule. Furthermore, phase

separation occurs more readily for a system having a 1:1 ratio of components (by volume) when the molecular chain length and number of blocks are kept constant. Phase separation is also improved by the incompatability between the two components so (δ_A - δ_B) is large.

A feature of both Meier's and Krause's work is the use of Hildebrand's solubility parameter. Studies conducted by McGrath et al (248) have served to illustrate the importance of the differential solubility parameter (δ_A-δ_B) or Δ and the chemical bond between the segments regarding the microphase separation in block copolymers.

Further theoretical treatments relating to domain formation and the state of the interface in block copolymers include those due to Helfand (249,250), Le Grand (251), Soen et al (252) and Bianchi et al (253,254).

5.15 Morphological Considerations in Block Copolymers

Microstructures on the size scale of polymer chains result when block copolymers undergo microphase separation due to thermodynamic incompatibility of the constituent blocks. The microstructural elements, rich in one block component, take the form of either spherical, cylindrical or lamellar domains dispersed in a continuous matrix of the other component. At compositions with approximately equal proportions of the two components, a lamellar structure is favoured. As the proportion of one component increases at the expense of the other, cylindrical morphologies will

result with the matrix phase being composed of the component in greater abundance. Increasing the proportion of one component further results in the morphology of spherical domains of the minor component in a matrix of the other component. These structures have been observed by Inoue et al (255) in diblock copolymers of isoprene and styrene cast from toluene. While the equilibrium morphology depends primarily on the bulk polymer composition, the phenomenon of microphase separation and the actual morphology are also functions of temperature, chemical potential, molar mass, molecular architecture (e.g. diblock, triblock etc) and formation history in general. Microphase configurations are responsible for the material's thermomechanical properties being different from those of both homopolymers and from those of a random copolymer of equal composition (256).

Combination of copolymers with homopolymers chemically identical to the blocks, leads to a more complicated situation. Early studies (257) claimed that if the molar masses of the homopolymer and its corresponding block are identical, or the former is not larger than that of the latter, the chains are miscible. However, Eastmond et al (258,259) demonstrated that in block copolymer-homopolymer blends the blocks and homopolymers are essentially immiscible even if their molar masses are comparable. Non-equilibrium morphologies were found to appear in these blends under suitable combinations of molecular species and processing conditions. In order to explain their formation

it was suggested that the homopolymer chains are incompatible with like blocks of copolymers at equilibrium and the discrete regions found in the blends are virtually the copolymer-rich phase. The unusual morphologies are formed by a combination of macrophase separation in the block copolymer itself. This was predicted by Meier (260).

5.16 Block vs Graft Copolymers

In a block copolymer, the monomeric sequences are joined end to end along the main chain of the molecule, whereas the molecules of a graft copolymer have a branched structure, one monomer forming the main chain 'backbone' and the other monomer forming the branches. However, many basic characteristics of block copolymers and graft copolymers are similar. This due to an important feature that they have in common, namely, the presence of intersegment chemical linkages. However, why greater emphasis should be placed on block copolymers rather than graft copolymers requires some explanation.

A high degree of structural control and integrity is necessary in order to achieve the ultimate properties inherent in microphase separated systems. It is in this respect that block copolymers have a clear advantage over graft copolymers. It is easier to synthesise block copolymers with controlled characteristics than it is to make graft copolymers. This results in a much better control of important parameters such as sequence architechture, segment length and spacing, polydispersity

and contamination by homopolymer or undesired copolymer architectures. These factors lead to a higher degree of morphological perfection in block copolymers than in graft copolymers.

The degree to which structural control is achieved can only be ascertained through the use of effective characterisation tools. The characterisation techniques traditionally used to analyse homopolymers can also be used in elucidating copolymer structures. Block copolymers are more difficult to characterise than homopolymers or polymer blends, and are usually contaminated to a minor degree with homopolymer. In addition, it is difficult to determine the block copolymer architecture (e.g.A - B versus A - B - A). However, graft copolymers are even more complex than block copolymers. While the number of segments in a block copolymer can be deduced with some certainty from the synthetic route adopted this is rarely possible with graft copolymers. This is because of the multifunctional nature of the backbone and the questionable efficiency with which these functionalities participate in the grafting reaction. The length of the graft segments and their polydispersity are also more difficult to determine for similar reasons. An important further complication is the question of the spacing of the graft junction points along the backbone. In block copolymers this parameter is more accessible. In A - B and A - B - A block copolymers there are by definition one or two junction points respectively. In $(A - B)_n$ block copolymers the distance between intersegment

linkages can be deduced from a knowledge of the block molar mass.

It may be concluded that although block copolymer synthesis can be more demanding than graft copolymer synthesis, the additional effort is usually more than rewarded by the excellent structural control obtained and the greater ease with which the structure may be characterised.

5.2 Experimental

5.21 Melt Blending of PBT - PDMS Block Copolymer in PBT Matrix

5.211 Copolymer/Matrix Blending Utilising Injection Moulder

Before processing the PBT - PDMS block copolymer (100g) and standard grade PBT(Arnite T 900g) were dried for twenty four hours at 110^{o}C in vacuo. The polymers were blended by passing through a Fox and Offord reciprocating screw injection moulder. The blend obtained was then regranulated and passed through the injection moulder a second time. This blend was then regranulated a second time and passed through the injection moulder a third time. Tensile test pieces and Izod impact specimens were formed this time.

The procedure was repeated for standard grade Arnite T without block copolymer present to give the same thermal treatment. The processing conditions for each sample are listed in Table 5.1.

TABLE 5.1 Processing Conditions for Copolymer and PBT Matrix

Model: Fox and Offord Unimould Screw Diameter 25.4 mm		
Mould Temperature	°C	90
Cylinder Temperature Settings		
Zone 1 (hopper)	°C	260
Zone 2	°C	255
Zone 3	°C	250
Nozzle Temperature Setting	%	100
Injection Pressure	psi	1000
Dwell Pressure	psi	1000
Screw Speed	rpm	130
Injection Time	s	1
Holding Time	s	20
Cooling Time	s	10
Total Cycle	s	36

5.212 Copolymer/Matrix Blending Utilising Brabender Plastograph

Before processing the polymers were dried in vacuo at 110°C for twenty four hours. Blending of PBT with block copolymers was performed using the Brabender Plastograph mixer at a temperature of 240°C ± 2°C in the mixing chamber. After softening the PBT in the mixing chamber, the motor was driven at 120 rpm for three minutes (constant torque was achieved during this period). The speed was then reduced to 50 rpm and the block copolymer added. After three minutes, during which time the copolymer melted, the speed was increased to 120 rpm. Mixing was continued for a further three minutes. The mixing head was then dismantled and the bulk of the material was removed as quickly as possible.

5.22 Tensile Testing

The stress-strain test is one of the most widely used mechanical tests. Usually this involves taking a standard-shape test piece (commonly a dumbbell) and extending it at a fixed strain rate until fracture. The force developed in the sample is automatically recorded. This leads to a "load-extension" curve which is usually transposed to a "stress-strain" curve. The tensile stress (σ) and the tensile strain (ε) are defined in equations (5.6) and (5.7).

$$\sigma = F/A_o \qquad \text{Eqn. (5.6)}$$

$$\varepsilon = (l - l_o)/l_o \qquad \text{Eqn. (5.7)}$$

F is the tensile force, A_o is the original cross-sectional area, l is the stretched length and l_o is the original length.

From the stress-strain curve a number of useful characteristic measurements of deformation behaviour can be obtained. The schematic diagram (Fig. 5.1) indicates such measurements e.g. yield stress, σ_y elongation at break ε_y, tensile strength σ_b, and elongation at break ε_b.

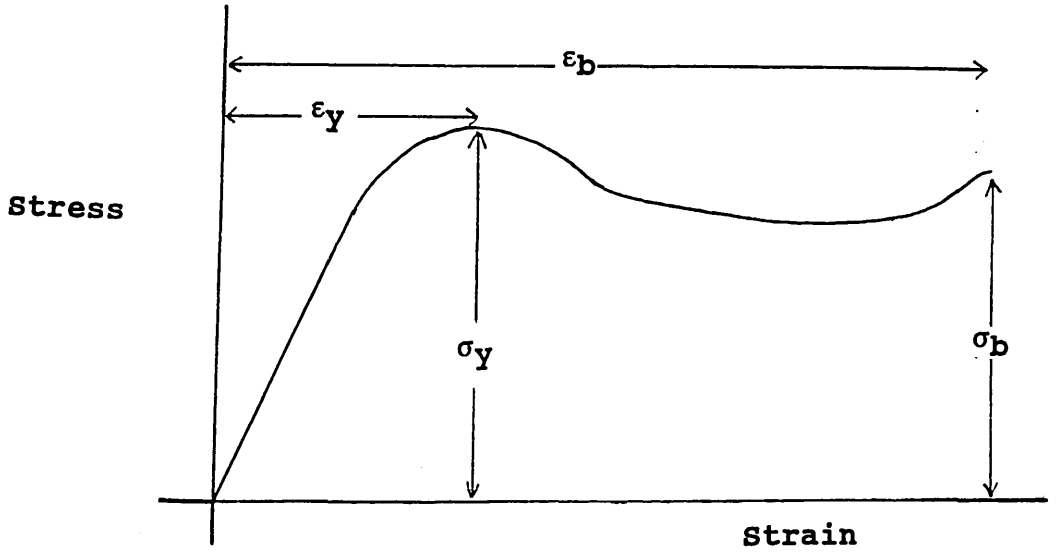


Fig. 5.1 Schematic Stress-Strain Curve for a Ductile Material

Various moduli (initial, 1%, 100% etc) can also be defined as follows. Modulus is defined as the stress at indicated strain over strain. The initial modulus is the slope of the very early part of the stress-strain curve.

Stress-strain measurements were performed using either a J.

J. Lloyd tensile testing instrument, type T5002 or a computer interfaced Nene tensometer. Injection moulded dumbbell samples were prepared for the Lloyd tensometer, while dumbbell shaped test pieces were cut from compression moulded plates for use with the Nene. The measurements were performed at ambient temperature and a strain rate of 6mm/min unless otherwise stated.

5.23 Electron Microscopy

Direct visual confirmation of the presence of two phases has been used more often (261) than any other technique as a preliminary indication of the degree of miscibility in a polymer - polymer system. If the rubber particles are large enough to be resolved by the light microscope, optical microscopy is the simplest and cheapest method for studying morphology. However, one drawback of the optical microscope is its relatively limited resolution. Most rubber toughened plastics have rubber particles that are too small to be seen and resolved in the optical microscope. Electron microscopy has become a valuable tool for more detailed observations of the morphology of polymer - polymer systems. A general comparison of microscopy techniques is shown in Table 5.2.

TABLE 5.2 Microscopy Techniques

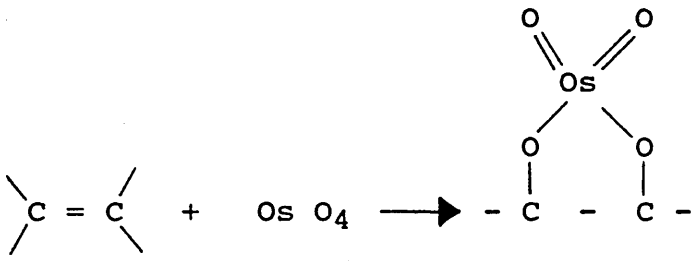
Type	Size Range	Magnification
Optical	1cm - 0.2 μm	1x - 1000x
Scanning	1cm - 5 nm	10x - 50,000x
Transmission	0.1mm - 0.3 nm	3000x - 5000000

Scanning electron microscopy (SEM) has become a standard method for examination of polymer surfaces. The surfaces to be examined can be prepared by microtoming, abrasive polishing or fracture. However, specimens for SEM need to be electrically conductive in order to produce secondary electrons and to minimise charge build up as polymers are generally non-conductive. To achieve this the sample is vacuum coated with a 20nm layer of gold or other suitable metal to prevent charging in the electron beam.

The copoplymer/matrix blend morphologies were examined by scanning electron micrographs of surfaces from cryogenically fractured samples. The specimens were prepared by immersing the sample in liquid nitrogen for three minutes before inducing brittle fracture. The fractured surfaces were evaporation coated with carbon before observation in the Philips scanning electron microscope model PSM 500.

Transmission electron microscopy (TEM) has been widely used (262) in polymer - polymer studies. For the passage of the electron beam, TEM requires much thinner specimens than those used in optical microscopy. The effective upper

limit is approximately 0.2μm. The necessary step of microtoming can be facilitated by cryogenic or chemical methods. A major problem with polymers sectioned for TEM is their inherent lack of contrast. Polymers have a low scattering power which results in low contrast. Methods that are employed to enhance contrast include staining, etching, replication, shadowing and metal decoration. Undoubtedly the most successful method for studying the morphology in rubber toughened plastics is the Osmium staining method developed by Kato (263,264). The basis of the method is the reaction between osmium tetroxide and the ethylenic unsaturation of a rubber to form a cyclic osmic ester (265,266).



This reaction has the dual effect of hardening the rubber, so that it is easier to section and providing electron contrast with the unstained matrix. Unfortunately this procedure is only applicable to polymers containing unsaturated rubbers.

TEM analysis was carried out on blocks cut from the copolymer/matrix blend with a fine saw and sectioned in a Porter-Blum ultramicrotome using a diamond knife. Sectioning was carried out at room temperature. Thin sections were mounted on 200 mesh copper grids previously

coated with a thin film of evaporated carbon. They were examined in a Hitachi HU - 11E electron microscope at 75 kV using a 50μ objective aperture. Attempts were initially made to harden and stain the materials with osmium tetroxide but with no apparent effect. Most of the contrast observed derives from the differential loss of one phase under the electron beam.

5.24 Notched Izod Impact Tests

The notched izod impact test is used to investigate the behaviour of PBT and copolymer modified PBT under specified impact stresses and to estimate the toughness of the specimens.

The experiments were performed using a Davenport pendulum impact testing instrument. Injection moulded Izod test specimens were prepared with the following dimensions $l = 50 \pm 2mm$, $y = 6.35mm \pm 0.1mm$ and $x = 6.35mm \pm 0.25mm$ Notches were machined with a fine tooth saw in accordance with Fig. 5.2.

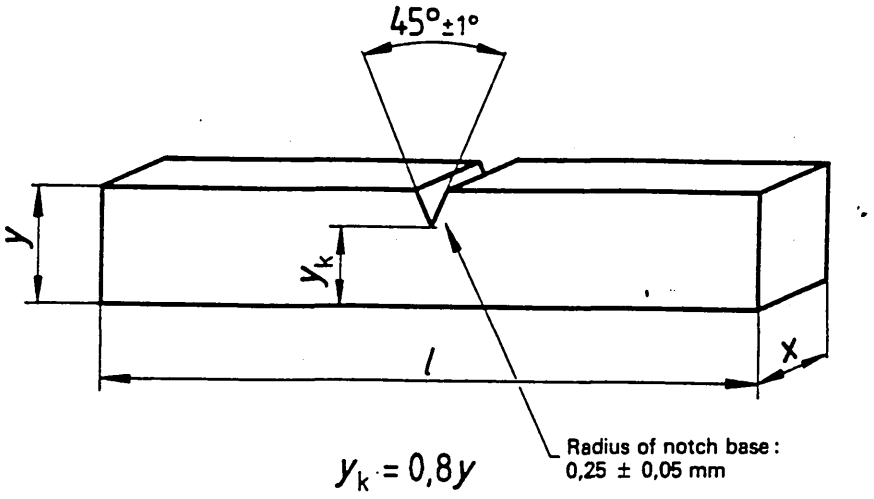


Figure 5.2 Notched Izod Test Specimen

The instrument was fitted with a pendulum of the correct energy range (1.36 J). A blank test was performed (i.e. without test piece in place) to ensure friction losses were within acceptable experimental error. The test piece was then measured accurately using a micrometer screw gauge, a number of readings being taken for each dimension to establish a mean value for the measurement. The pendulum was lifted and secured in the starting position and the pointer adjusted so it touched the driving pin. The test piece was placed in the vice and clamped with the notch positioned such that it was to be struck by the striking edge of the pendulum (see Fig. 5.3).

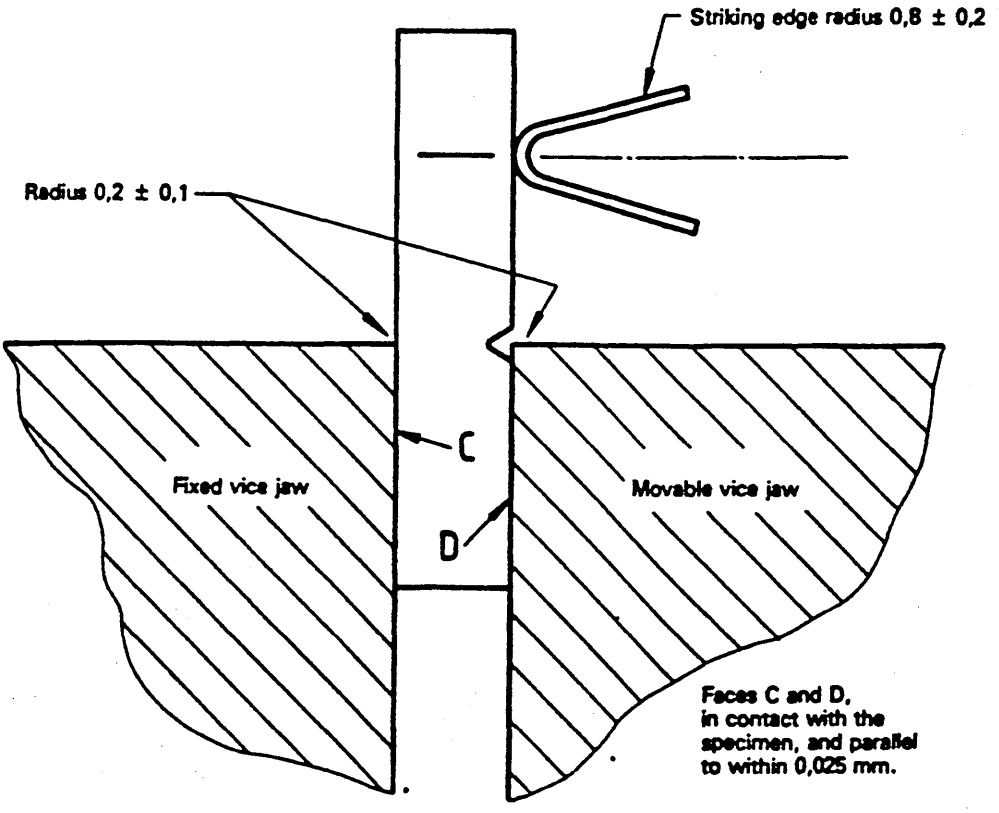


Figure 5.3 Vice Support and Test Specimen

(notch and striking edge shown in normal position)

The pendulum is carefully released and the impact energy absorbed by the specimen read from the scale. The Izod impact strength of notched specimens was calculated using the following equation:

$$\text{Impact Strength} = \frac{12.7\ E\ Y}{(10\ W)} \qquad \text{(Equn. 5.8)}$$

where:

Impact strength is in J per 12.7mm width of specimen

E = Arithmetic mean of energy absorbed by sample

Y = Energy of pendulum used (J)

W = Nominal width of specimen

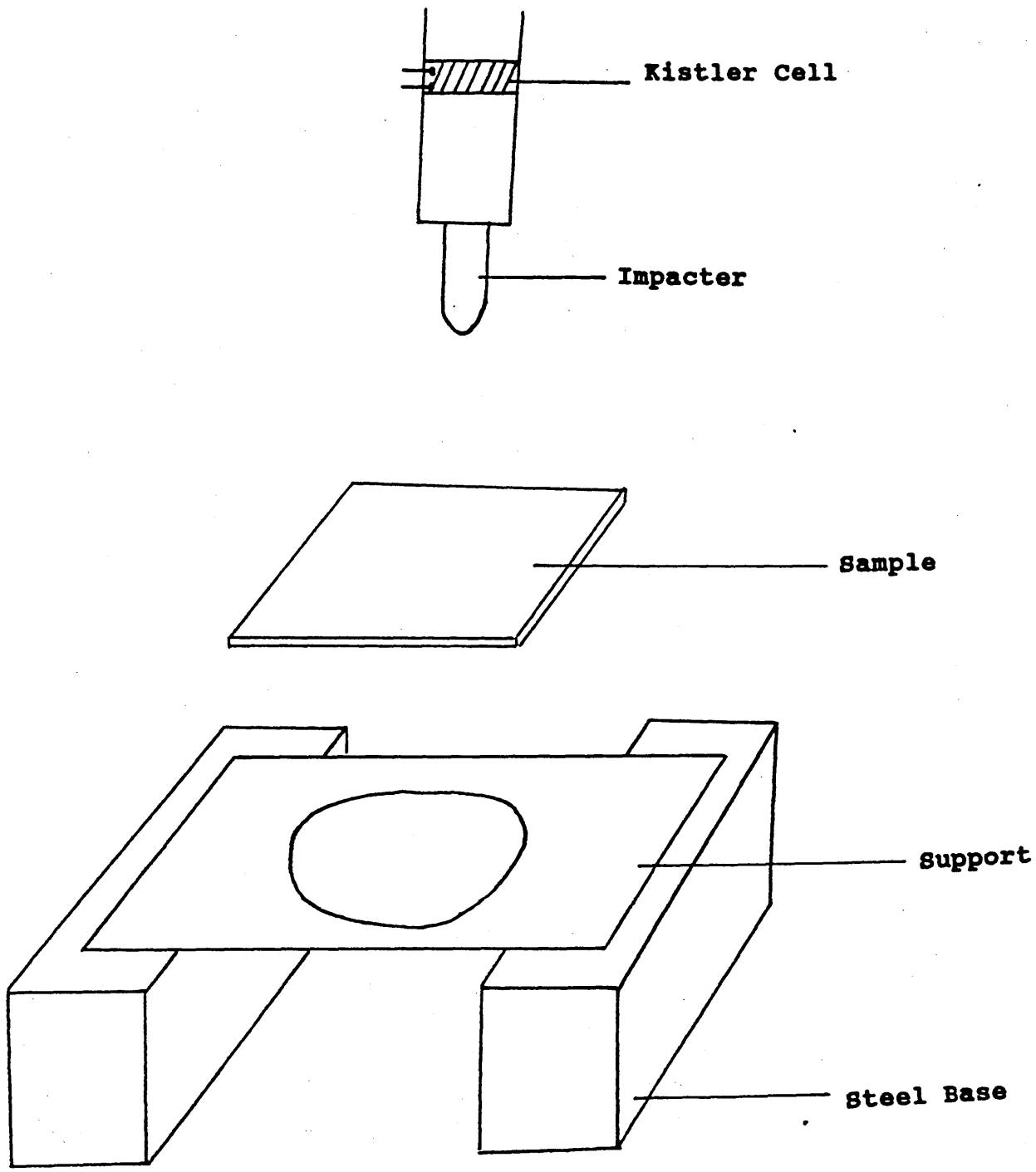
To convert impact strength from J to Jm^{-1} multiply by (1000/12.7)

5.25 Falling Weight Impact Tests

Falling weight impact tests were performed utilising a Rosand computer interfaced impact tester. Test pieces of dimensions 6cm x 6cm x 2mm (+ 0.1mm) were cut from compression moulded sheets (12 x 12cm) and were supported as shown in Fig. 5.4.

The impacter has a mass of approximately 4.8kg and strikes the sample with a velocity of $3.0ms^{-1}$. The energy absorbed at impact is translated by the computer and force displacement curves are produced. All measurements were carried out at $20^{o}C \pm 1^{o}C$.

Figure 5.4 Schematic Representation Of Rosand Impact Tester.



5.3 Results and Discussion

5.31 Copolymer/Matrix Blend Preparation

Two different instruments were used to melt blend the copolymer with PBT, i.e. an injection moulder and a Brabender Plastograph. Initially the injection moulder was used to process the blend. However, the Brabender offered two main advantages;

1) Smaller mass of sample required. Appromimately 60g as compared to a minimum of 1kg for injection moulder.

2) Shorter processing time. The twin co-rotating screws of the Brabender ensured efficient mixing in the ten minutes the blend resided in the mixing chamber. The injection moulder required a minimum of three passes plus regranulating between each pass to create the required mixing.

Exposed to the air, PBT granules rapidly absorb moisture, as shown in Fig. 5.5, where the moisture content of granules in air of 23^{o}C and 50% RH has been plotted against time.

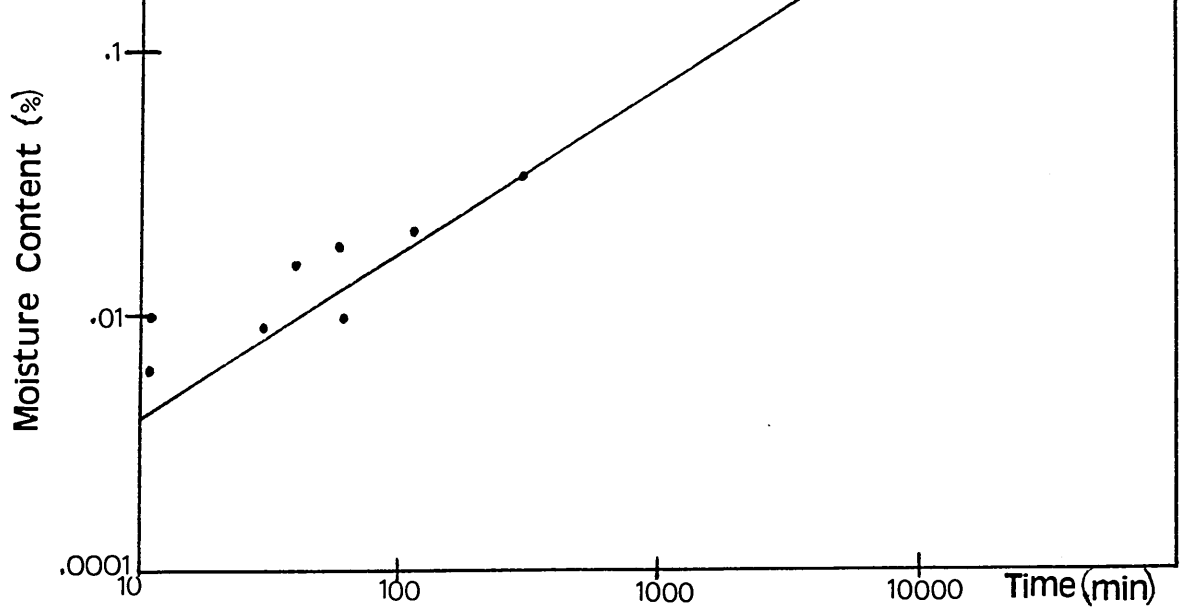


Figure 5.5 Moisture Absorption Of PBT Versus Time

Therefore, prior to blending using either method, granules of both matrix and copolymer were thoroughly dried in a vacuum oven. By nature thermoplastic polyesters in the molten state are susceptible to hydrolysis under the influence of moisture. Saponification occurs as small amounts of moisture react immediately, breaking the molecular chain and resulting in lower molar masses. Obviously viscosity decreases occur along with concurrent deterioration in properties. Fig. 5.6 shows the effect of moisture on three different thermoplastic polyester grades. It is therefore necessary that the moisture content of the granules is as low as possible.

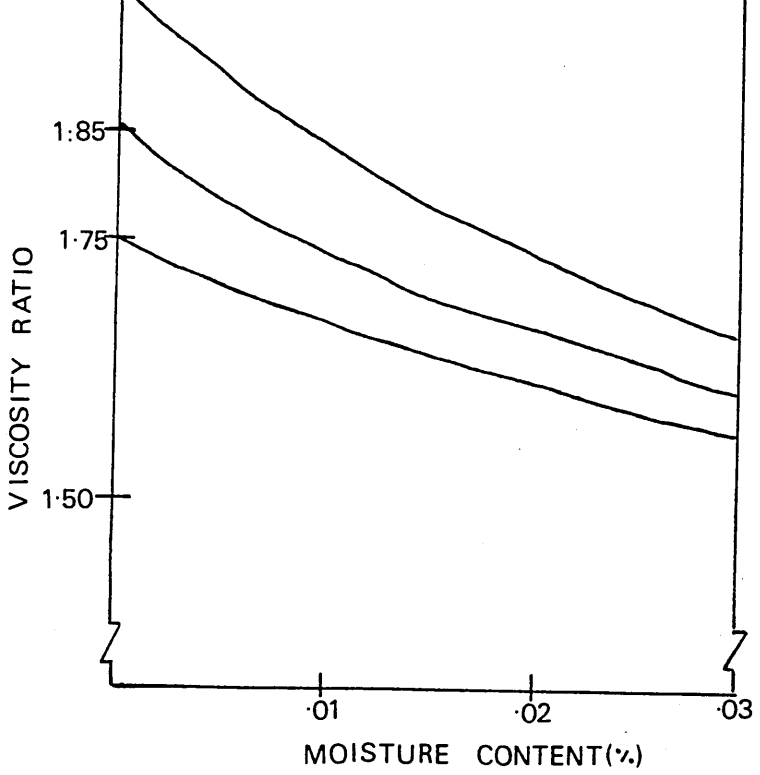


Figure 5.6 Influence Of Moisture On The Viscosity Ratio Of Thermoplastic Polyester(267)

Although PBT has good thermal stability the residence time of the polymer in the barrel of the injection moulder or the mixing chamber of the Brabender was kept to a minimum (less than fifteen minutes in each case). Similarly the temperature of the barrel zones and the mixing chamber were controlled to ensure the correct operating temperature. The processing temperature was kept at a maximum of 260°C in order to minimise transesterification and pyrolysis of PBT (162,163). Exposure to very high processing temperatures and /or long residence times favours thermal degradation. This was illustrated by observing the rheological behaviour of PBT melts using a Rheometrics Dynamics spectrometer (268). It was shown that when increasing the melt temperature gradually over an hour to 270°C and then returning to 240°C, the effect of holding

the melt at elevated temperature for an hour was to reduce the viscosity considerably. This is shown in figure 5.7.

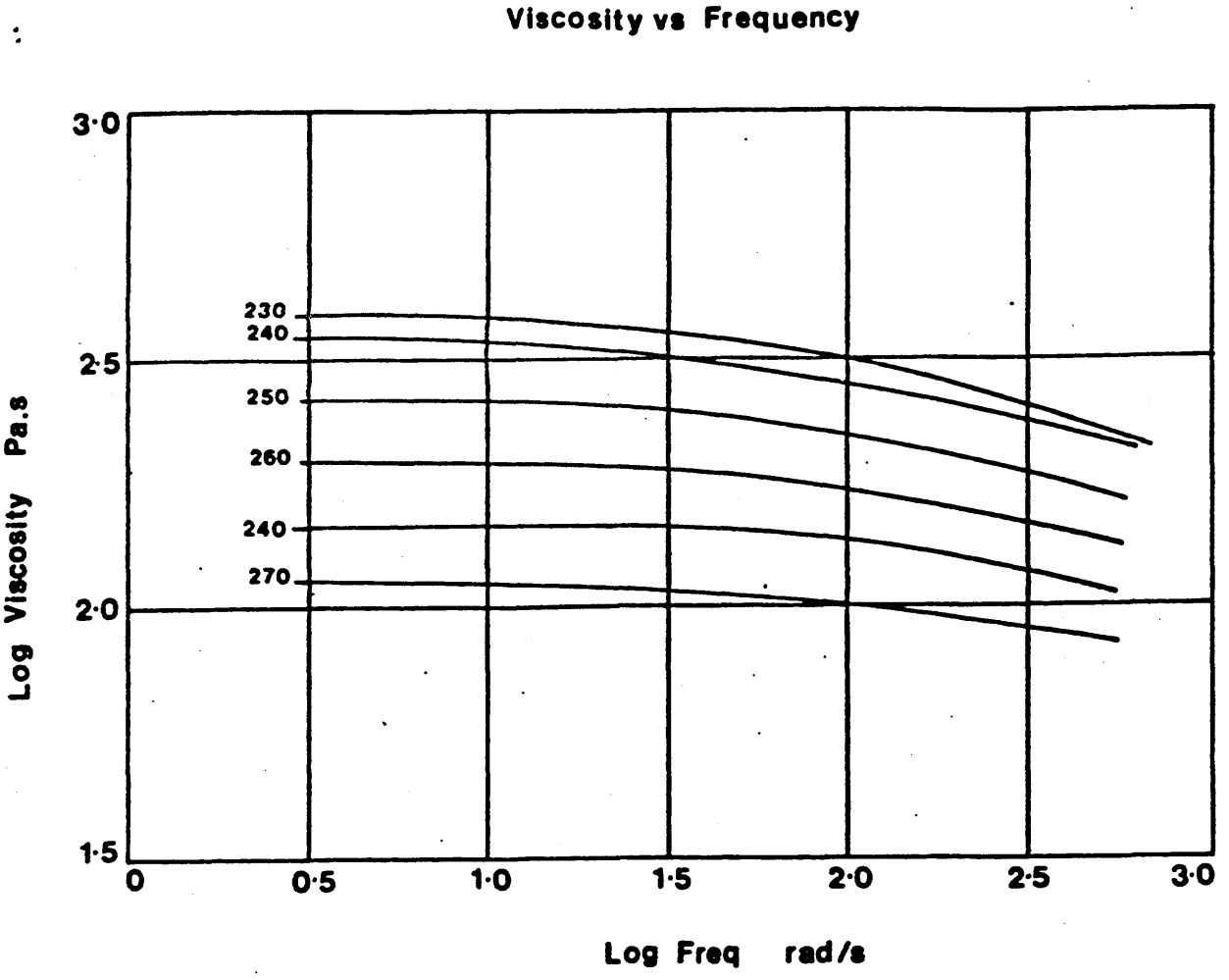


Figure 5.7 Variation Of Viscosity With Angular Frequency For PBT, Showing The Viscosity Reduction Caused By Elevated Temperature For One Hour

During the blending process a couple of differences were noticed between the processing characteristics of PBT compared to the PBT/copolymer blend.

1) As expected the viscosity of the blend was lower than that of the PBT matrix. This is predominantly due to the dilution effect of adding the low molar mass impact modifier. However, a secondary contribution will be due to transesterification that will occur at 240°C between the copolymer and the PBT matrix resulting in lower molar mass PBT chains and consequently lower viscosity.

2) The molten blend of PBT and copolymer showed a degree of opacity which was not apparent in molten PBT. This is assigned to a degree of incompatability between PBT and the copolymer,

The reduced viscosity of the blend caused the injection pressure to be lowered (to 800psi) when moulding to prevent flashing. The reduced viscosity was not a problem with the Brabender since test pieces were cut from compression moulded samples of the blend.

5.32 Mechanical Properties of PBT/Copolymer Blend

The first copolymer sample to be investigated as an impact modifier was synthesised by the method outlined in 4.233, a 50/50 m/m segmented copolymer of initial RMM PBT (2000) and PDMS (1000). This material was blended with standard grade PBT (10% w/w) and tensile and Izod test pieces were injection moulded. The same procedure was repeated for standard grade PBT for comparative purposes.

The tensile results obtained are shown in Fig. 5.8, and Table 5.3 and are an average of the best three results obtained from a sample size of 10. The blend of the block copolymer with PBT shows a decrease in both tensile strength and elongation as compared with standard PBT.

TABLE 5.3 Tensile Data for PBT/Block Copolymer Blends

Sample	Tensile Strength * Nmm^{-2}	Elongation * at break %
PBT	57.6	16
PBT/Block Copolymer Blend	50.2	11

Strain rate = 6mm/min

* - Average of best three results

Block Copolymer = PBT-PDMS 50/50 m/m Sn(II) Octoate as Catalyst

Results for impact testing the same experimental sample using notched izod specimens are given in Table 5.4. Again there is a decrease in the notched Izod impact strength at ambient temperature, for the PBT/copolymer blend in comparison with PBT.

Figure 5.8 Tensile Data For PBT And PBT/PDMS Block Copolymer Blend

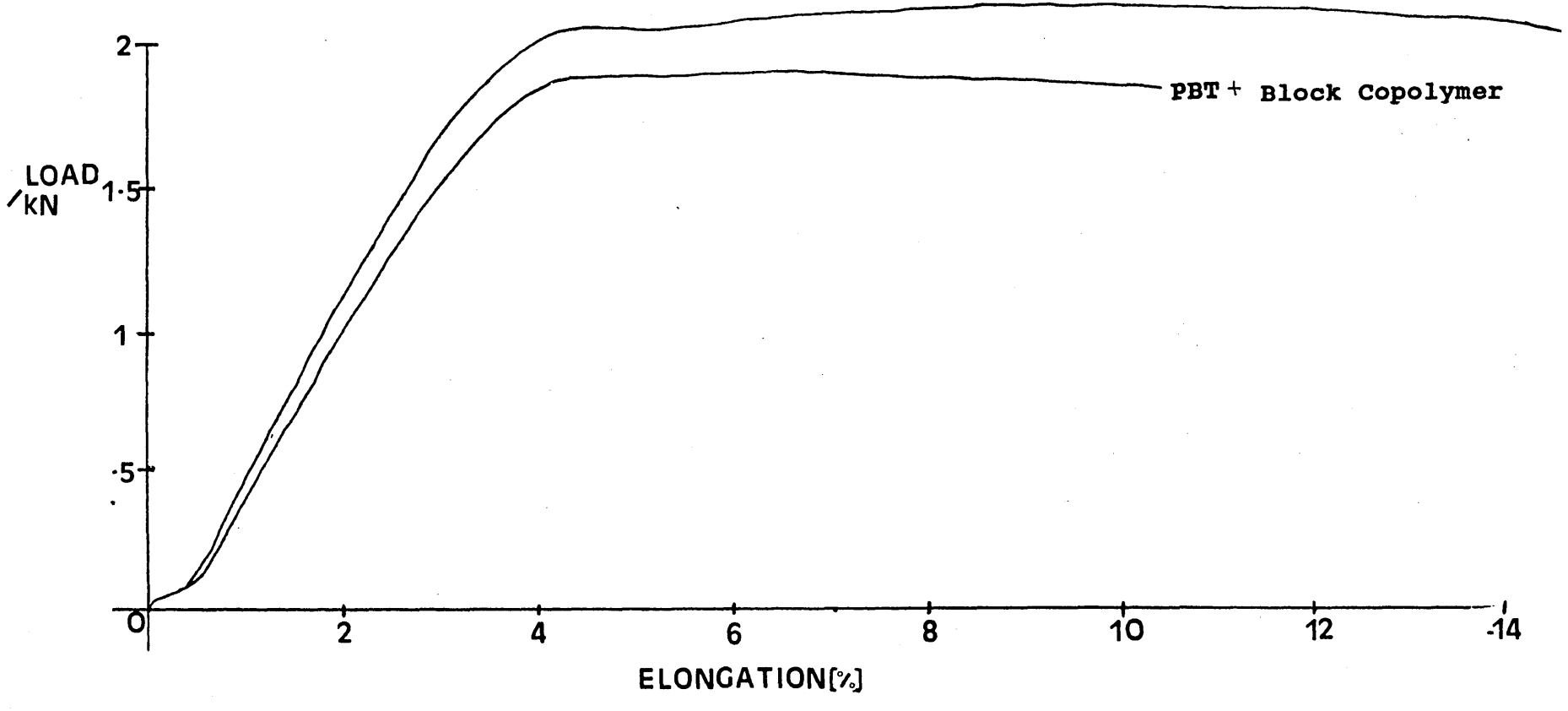


TABLE 5.4 Notched Izod Impact Strength Data for PBT/Block Copolymer Blend

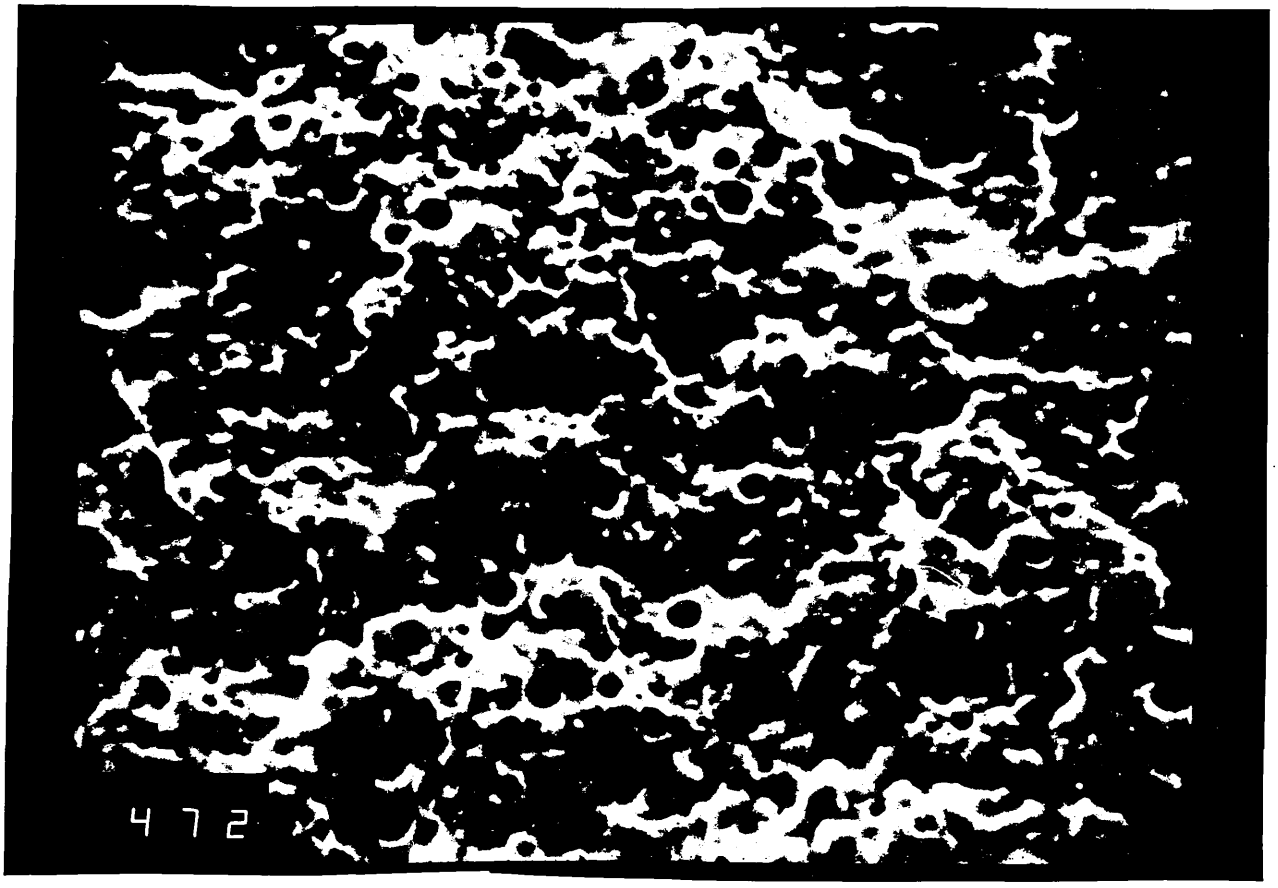
Sample	Impact Strength Jm^{-1}
PBT	24.8
PBT/Block Copolymer Blend	22.7

The decrease observed in the tensile strength and impact strength for the blends may be explained by the particle size of the rubber phase. Small particles can be inefficient in terminating crazes, whereas larger particles can hinder the cold drawing of the matrix and render it more likely to brittle failure. Thus a premature rupture of the specimen will occur. Poor rubber particle adhesion to the matrix will also aid in rapid failure of the specimen.

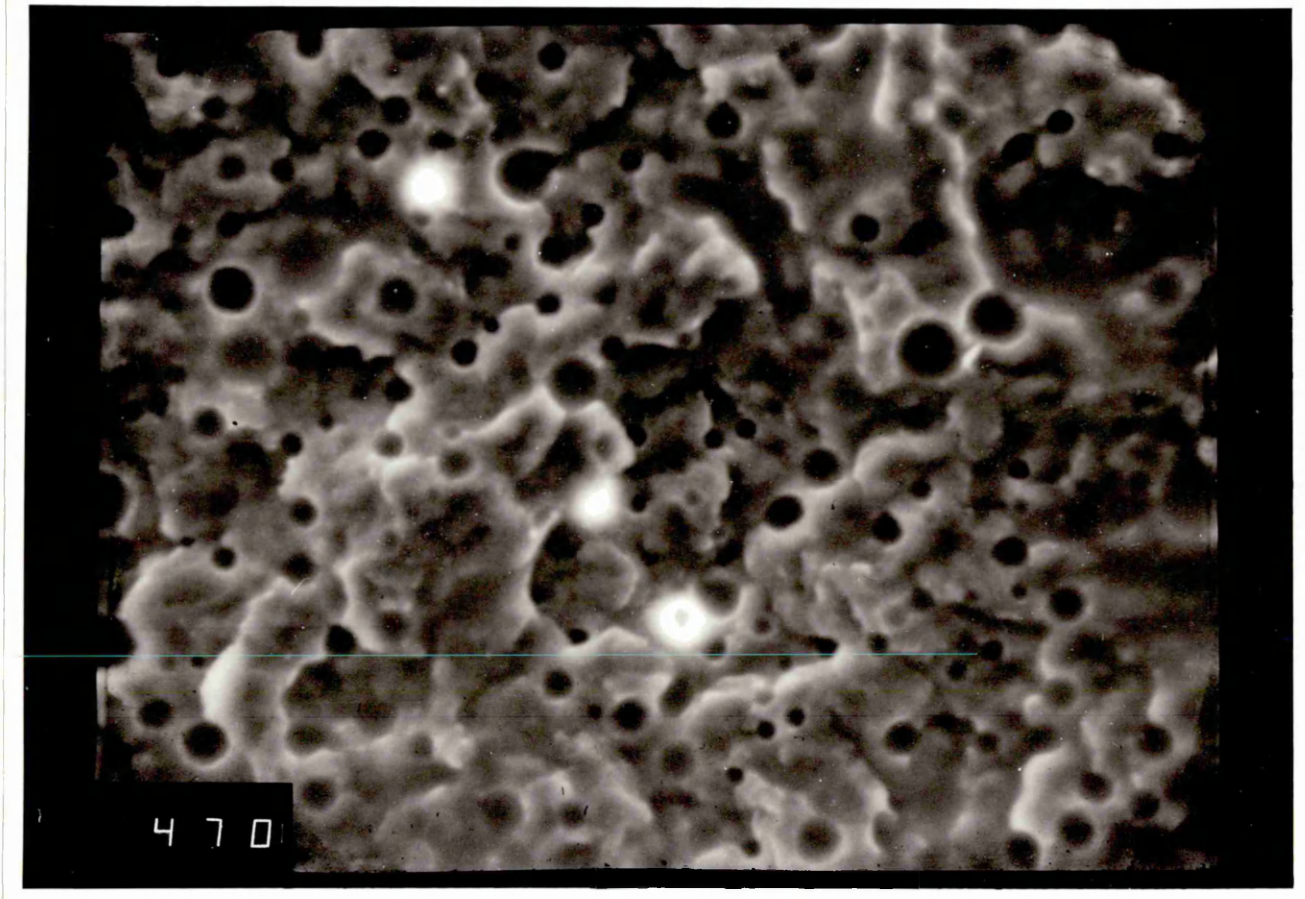
To further explain both the tensile behaviour and Izod results a morphological investigation was performed on cryogenically fractured sample surfaces analysed by scanning electron microscopy (SEM) and on microtomed surfaces analysed by transmisson electron microscopy (TEM).

The SEM investigation proved inconclusive but appeared to indicate that the rubber particles were of a very small size. Micrographs of the unprocessed blend (micrographs 1-3) indicate no obvious rubber toughening particles. However, examination of the silicon maps (micrographs 4, 5)

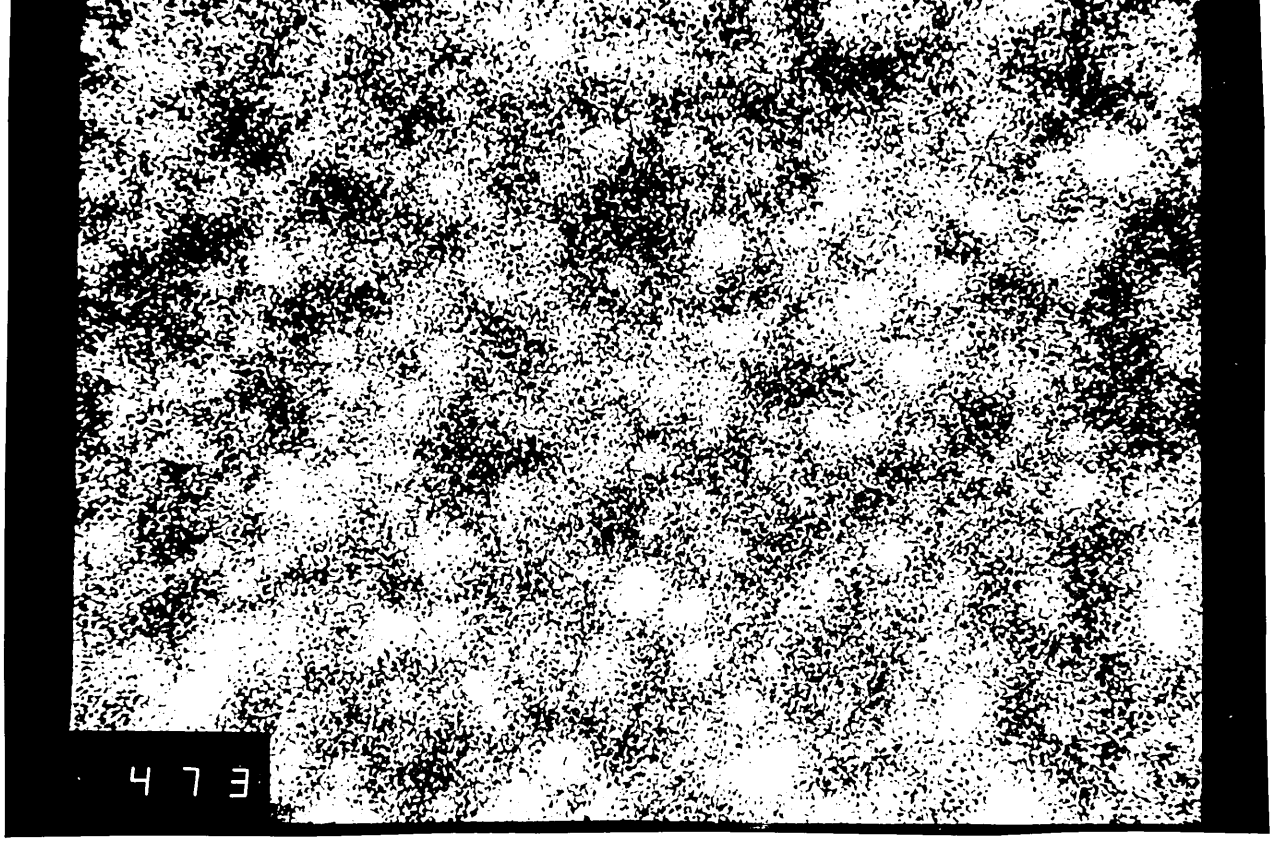
Micrograph 1 Unprocessed PBT/PDMS Block Copolymer Blend. Brittle Fracture Relief Magnification x 90



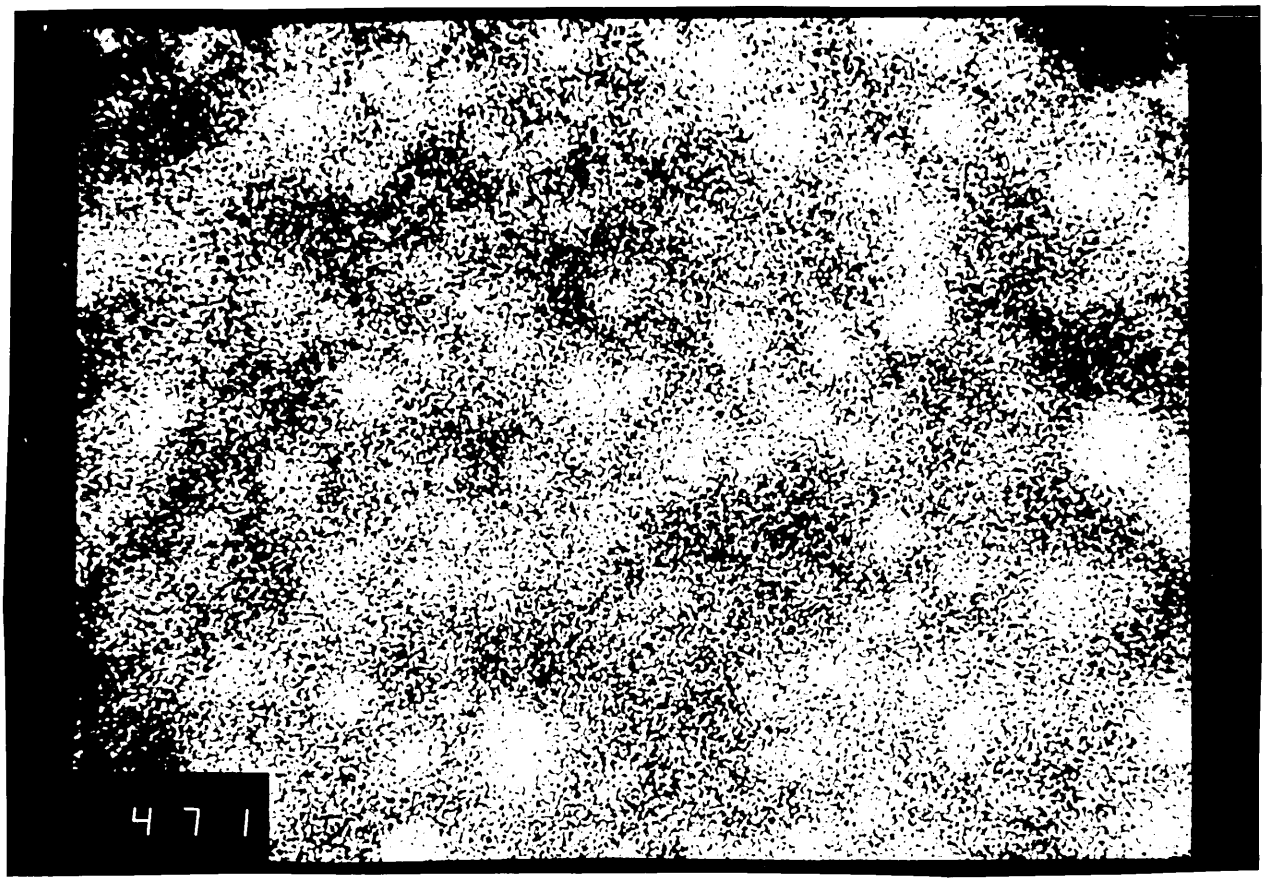
Micrograph 2 Unprocessed PBT/PDMS Block Copolymer Blend. Brittle Fracture Relief Magnification x 720



Micrograph 3 Unprocessed PBT/PDMS Block Copolymer Blend. Brittle Fracture Relief Magnification x 1440



Micrograph 4 Unprocessed PBT/PDMS Block Copolymer Blend. Silicon Map Of Micrograph 2 Magnification x 720

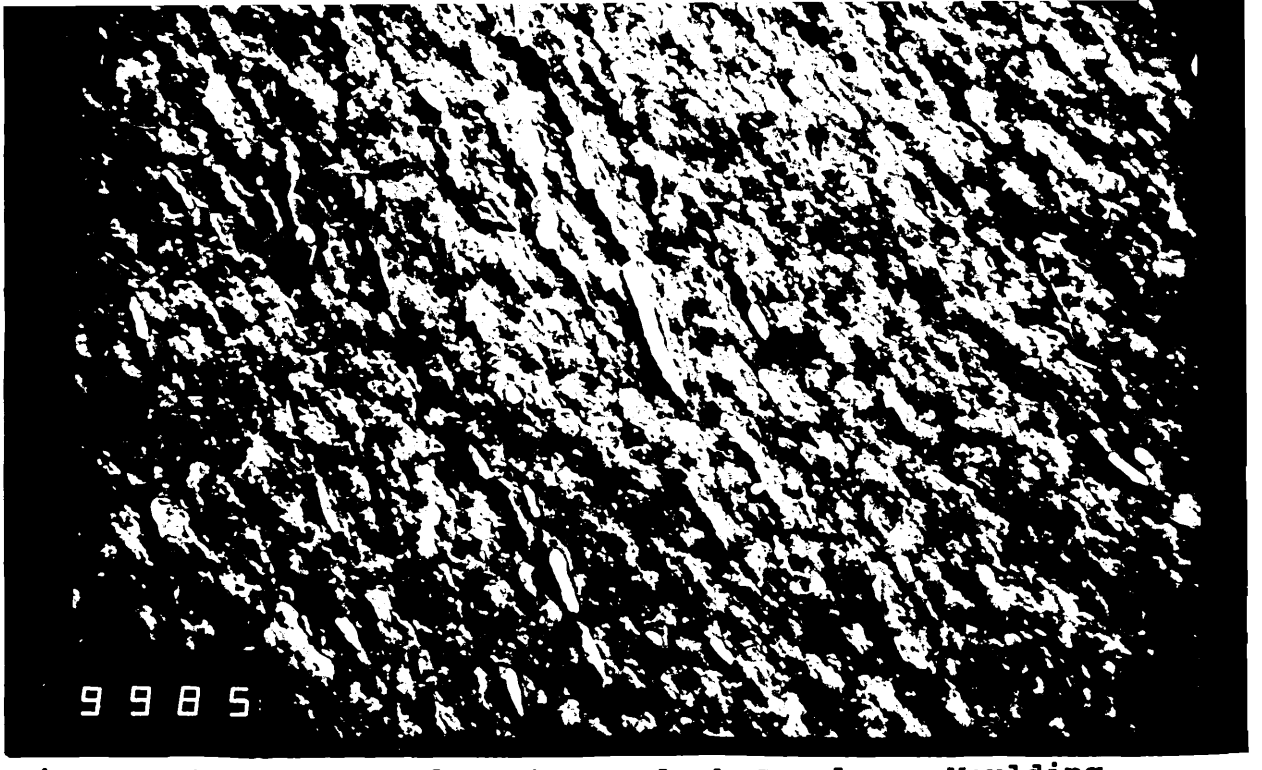


Micrograph 5 Unprocessed PBT/PDMS Block. Silicon Map Of Micrograph 3 Magnification x 1440 . Light parts representative Si

suggest a definite distribution of silicon exists even though the particles do not appear on the fracture relief micrographs. The particles have an average diameter of 4.2 $\pm$ 0.3μm and are assumed spherical. After processing though, rubber particles are not readily identifiable (micrograph 6,7) and elemental mapping (micrograph 8) shows what appears to be a very fine distribution of silicon content across the feature but with no rubber particles of note. This apparent fine distribution of silicon though is not much greater than the noise level obtained for a standard PBT sample (micrograph 9).

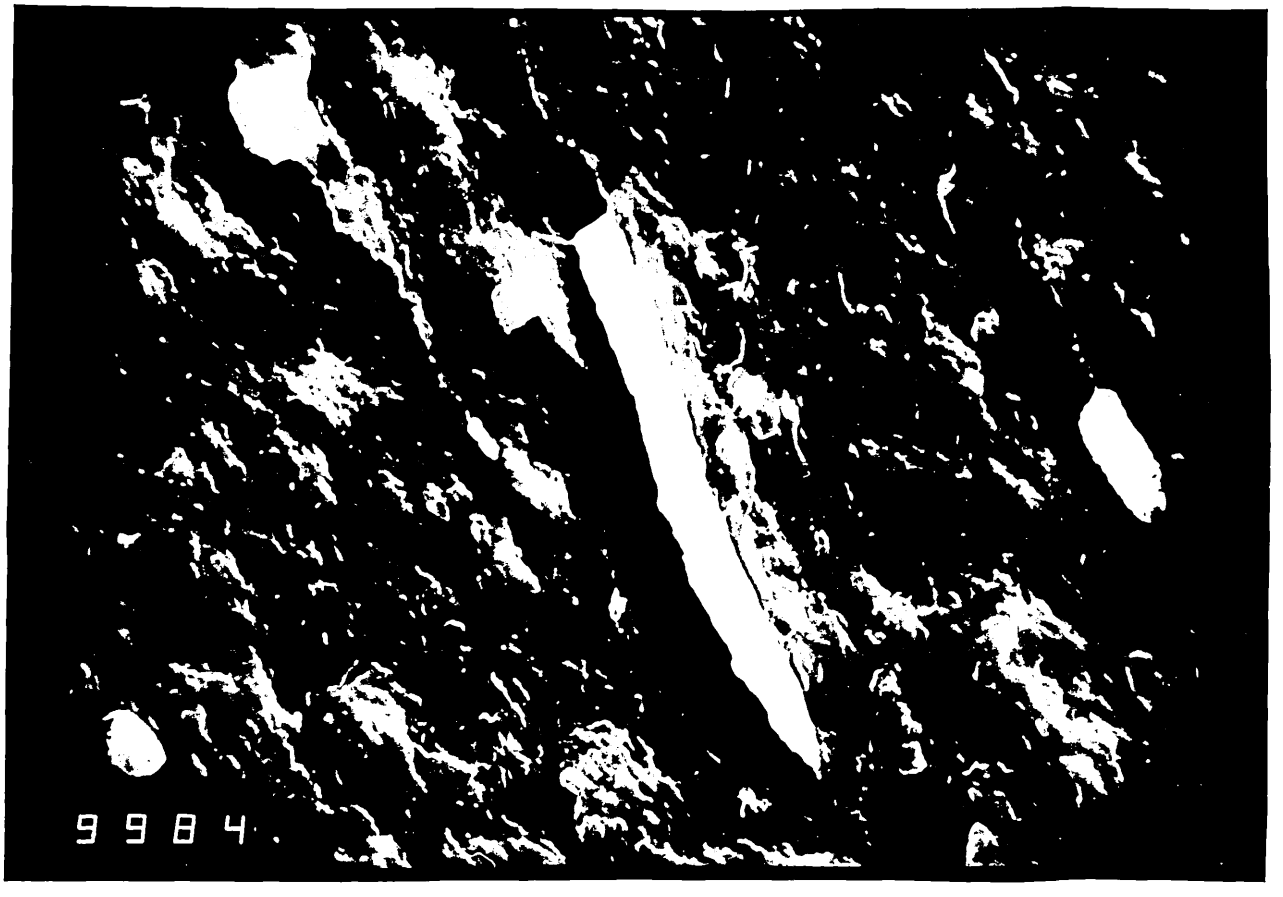
It would appear that the high shear forces the blend experiences in further processing and eventually in the injection moulding of the blend is responsible for the fine distribution of rubber particles. The silicon particles observed in the unprocessed blend are likely to be an agglomeration of a number of rubber species which are separated on further processing.

TEM results of the processed blend support the observation that the rubber particles are very small. Rubber particles of the size of 0.1 - 0.2 μm are identified (micrograph 10). Although polymer blends are characterised by only a small level of contrast between phases, therefore usually require staining, exposure of the copolymer/matrix microtomed sections to the electron beam caused an increase in contrast suggesting the differential loss of one phase,



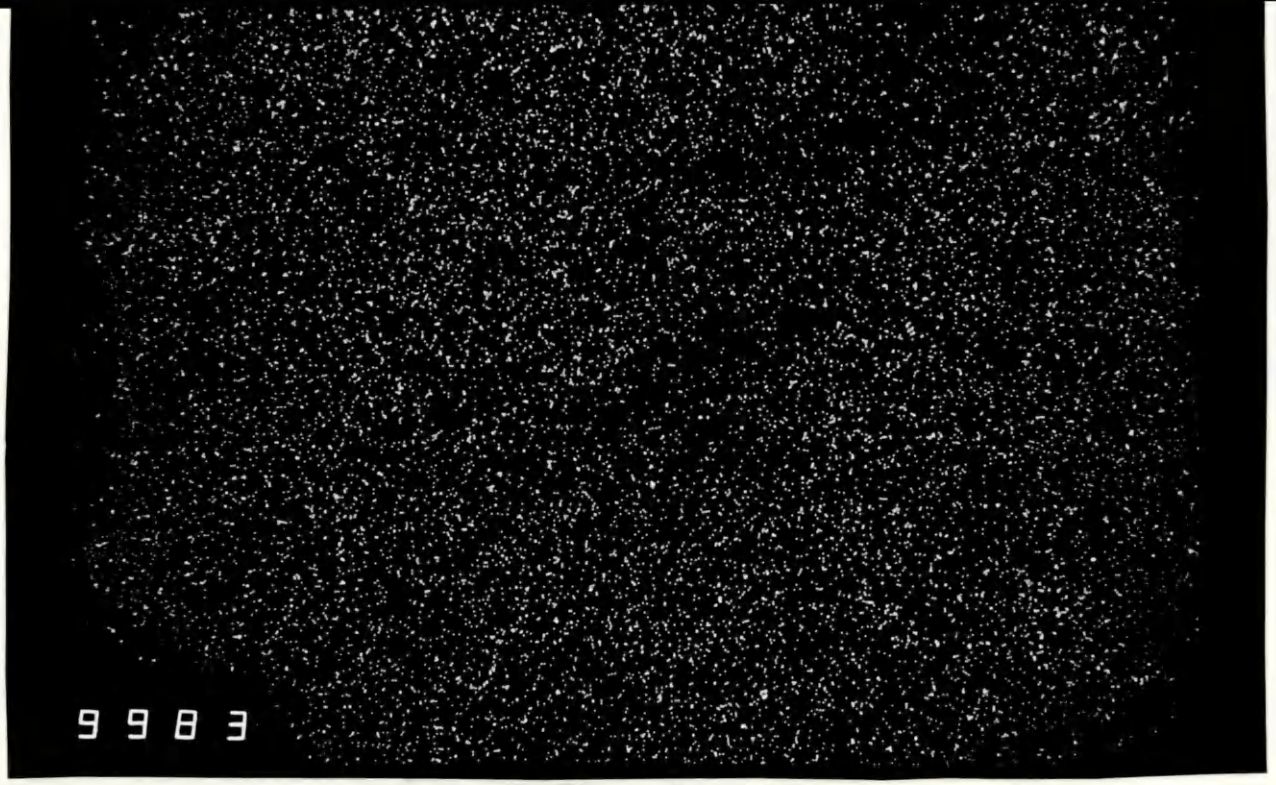
Micrograph 6 Processed PBT/PDMS Block Copolymer Moulding.

Brittle Fracture Relief Magnification x 340



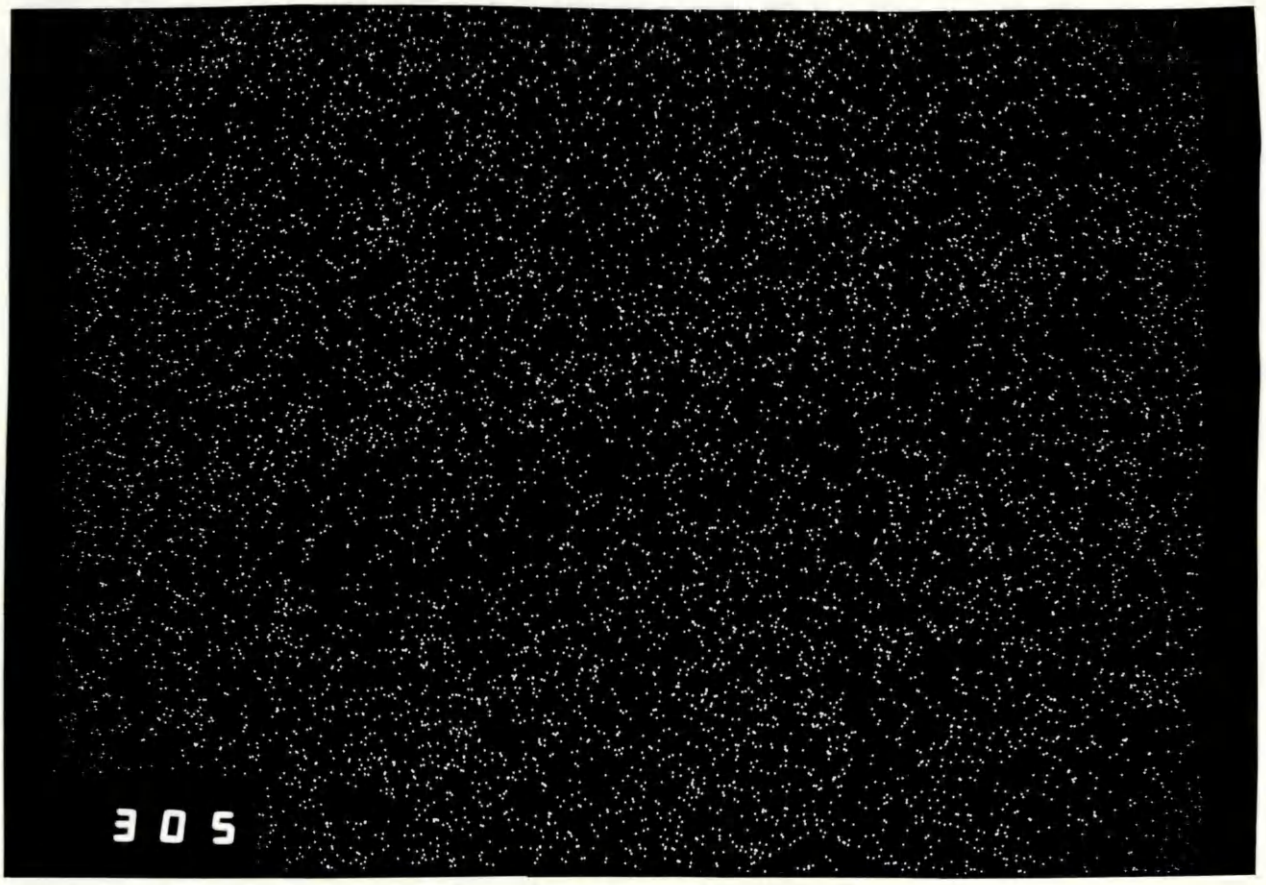
Micrograph 7 Processed PBT/PDMS Block Copolymer Moulding.

Brittle Fracture Relief Magnification x 1360

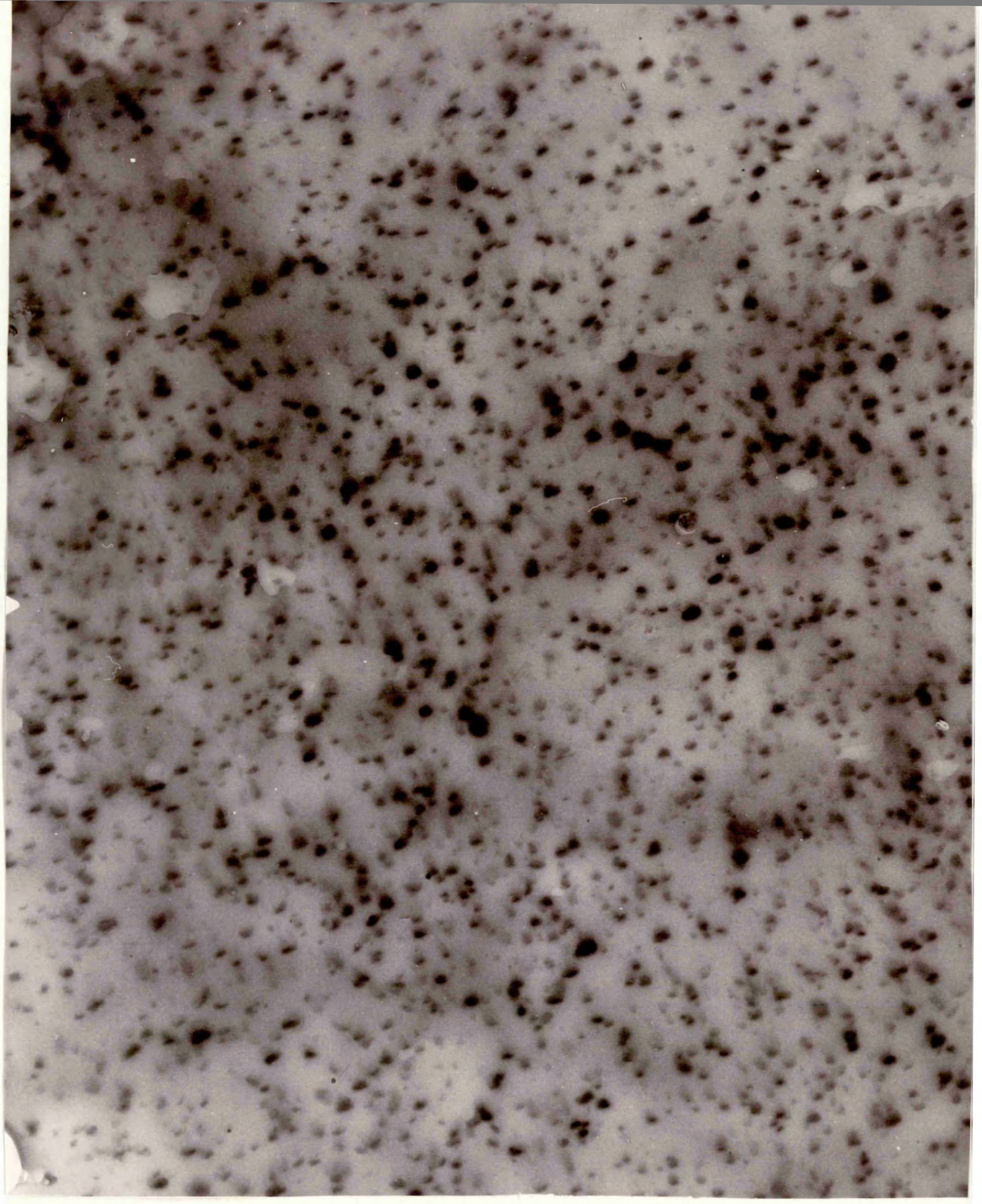


Micrograph 8 Processed PBT/PDMS Block Copolymer Moulding.

Silicon Map Of Micrograph 7 Magnification x 1360



Micrograph 9 PBT Moulding. Silicon Map Magnification x 800



1μm

Micrograph 10 PBT-PDMS 50/50 m/m Block Copolymer

(10%) Dispersed In PBT Matrix Magnification x 18000

assumed to be the rubber phase.

At high deformation rates, PBT fractures by a crazing mechanism (5,269,270). First voids are produced at spherulite boundaries. Crazes are formed from these very small voids, hence the role of the rubber inclusions is to both initiate and to terminate such crazes. These effects are accomplished most efficiently when the size of the rubber particles is in the range of 2 to 4 μm (18,29,30). Therefore the lack of toughening observed in the copolymer/matrix blend as compared to standard PBT may be explained to some extent by the rubber particles being too small.

5.33 Mechanical Properties of PBT - PDMS (50/50 m/m) Copolymers

A further contribution to the observed reduction in mechanical properties could be from the inherent mechanical properties of the block copolymer. The initial copolymer had been synthesised without any significant polycondensation period and was therefore of relatively low RMM (~ 2,500), and hence of poor mechanical properties. A polycondensation period of two to three hours was expected to increase the RMM and improve mechanical properties. A similar procedure had been used successfully in the commercial polyether-polyester copolymers (168). Stannous octoate had proved successful in forming the low RMM copolymer and was employed again. However, although copolymers were synthesised using different periods of

polycondensation it was observed that products with poorer mechanical properties were being obtained after longer polycondensation periods.

The results of the tensile experiments are given in Table 5.5 and Figure 5.9. The products all show poor extension. This is especially noticeable for the products after a two hour polycondensation period. Tensile strength is also considerably lower for this sample as compared to the others.

TABLE 5.5 Tensile Data for PBT/PDMS BCP's Synthesised Using Stannous Octoate as Catalyst

Sample Details	* Tensile Strength/mPa	* Elongation at break %	Area to end/J
BCP I Vac. 10 mins @ 10 mmHg	6.41	13.98	0.078
BCP II Vac. 30 mins @ 0.1 mmHg	6.26	12.80	0.045
BCP III Vac. 60 mins @ 0.1 mmHg	7.37	15.59	0.106
BCP IV Vac. 120 mins @ 0.1 mmHg	3.74	6.67	0. 03

Strain Rate = 10mm/min. * average of three best results

The results for the product obtained after one hour polycondensation period are probably a false representation of the true mechanical properties. This is because when the sample was initially hot pressed a liquid (presumably

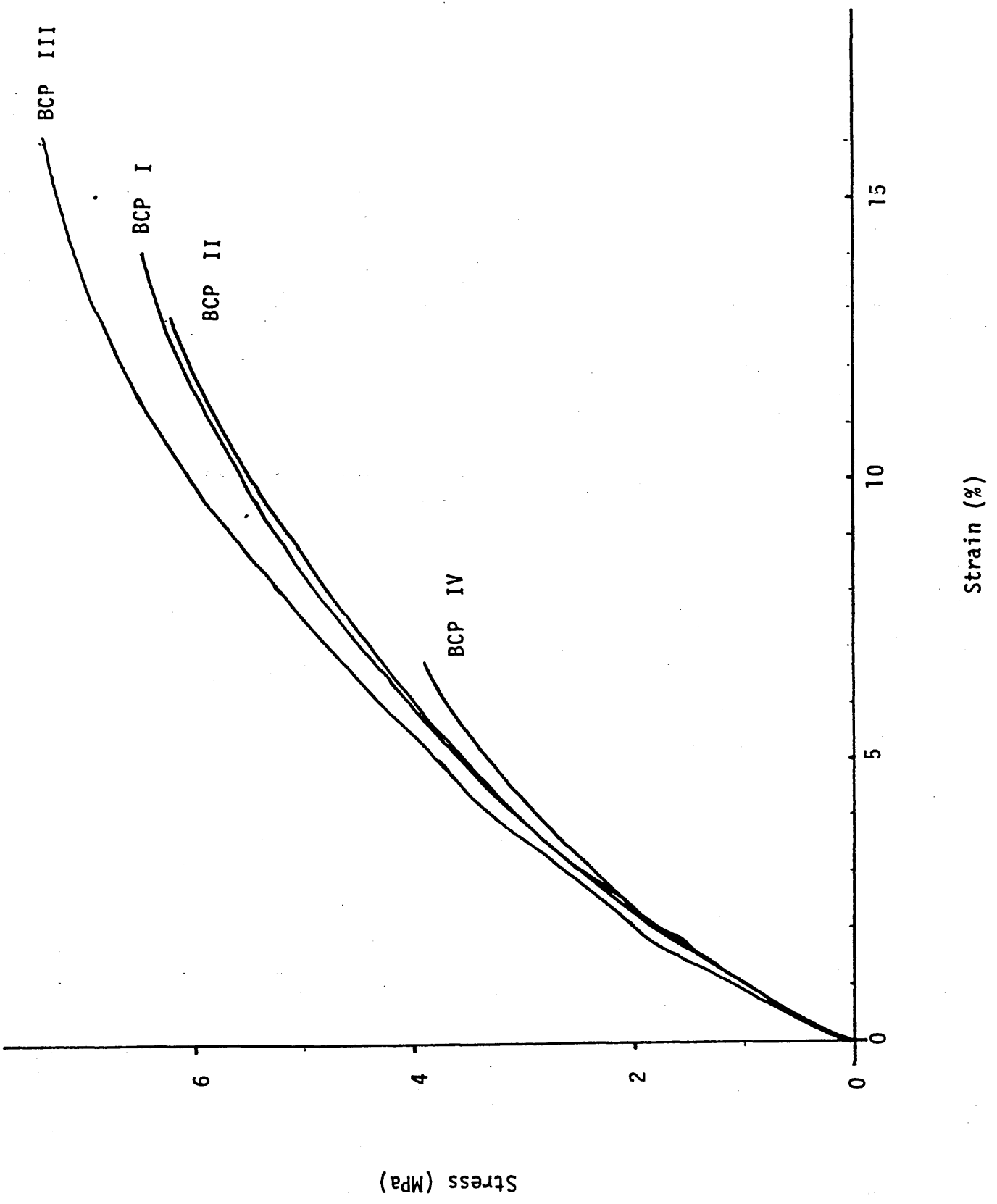


Figure 5.9 **Stress-Strain Curves For PBT-PDMS Copolymer (50/50 m/m) Sn Catalysis**

PDMS) leached out of the plates.

The first sample was so weak it crumbled on removal from the mould. On reducing the moulding time from five minutes to one minute, an acceptable sample was obtained with little leaching occurring. However, the sample was not uniform which is reflected in the data of the ten test samples. This leaching phenomenon was observed to a greater degree with the product obtained after a two hour polycondensation period.

Leaching is further support for the formation of high RMM PDMS, which occurs because stannous octoate catalyses the condensation of α,ω hydroxy PDMS the details of which were discussed in section 4.3. Obviously the longer the reaction period the greater the chance of forming high molar siloxane, and it is noticeable that significant leaching only occurs in samples of one to two hour polycondensation periods. Therefore we see a decrease in mechanical properties and increased leaching the longer the reaction period.

5.34 Effect of Composition on Mechanical Properties of PBT - PDMS Copolymers

Early block copolymer synthesis predominately concentrated on a 50/50 m/m copolymer composition. However, this composition as observed did not prove ideal and a number of routes to improving the mechanical properties of the copolymer were investigated.

Initially a 67/33 m/m ratio PBT - PDMS copolymer was synthesised together with the converse ratio i.e. 33/67 m/m ratio PBT - PDMS copolymer. Copolymers of each ratio were synthesized both with and without a significant polycondensation period. The tensile properties of these materials were assessed and the results reported in Table 5.6 and Figure 5.10.

TABLE 5.6 Tensile Data for PBT - PDMS Copolymers of Different Composition

Sample No.	Tensile Strength(MPa)	Elongation (%)	Youngs Modulus(MPa)	Area to End(J)
1	6.41	13.98	64	0.078
2	3.74	6.67	82.12	0.03
3	18.08	23.13	162.7	0.41
4	22.56	13.19	362.7	0.28
5	6.67	45.62	45.2	0.29
6	5.32	15.41	58.2	0.062
7	5.48	18.77	46.5	0.079
8	18.47	93.58	157.0	2.19

All values are the average of the strongest three samples tested. Strain rate = 6mm min^{-1}.

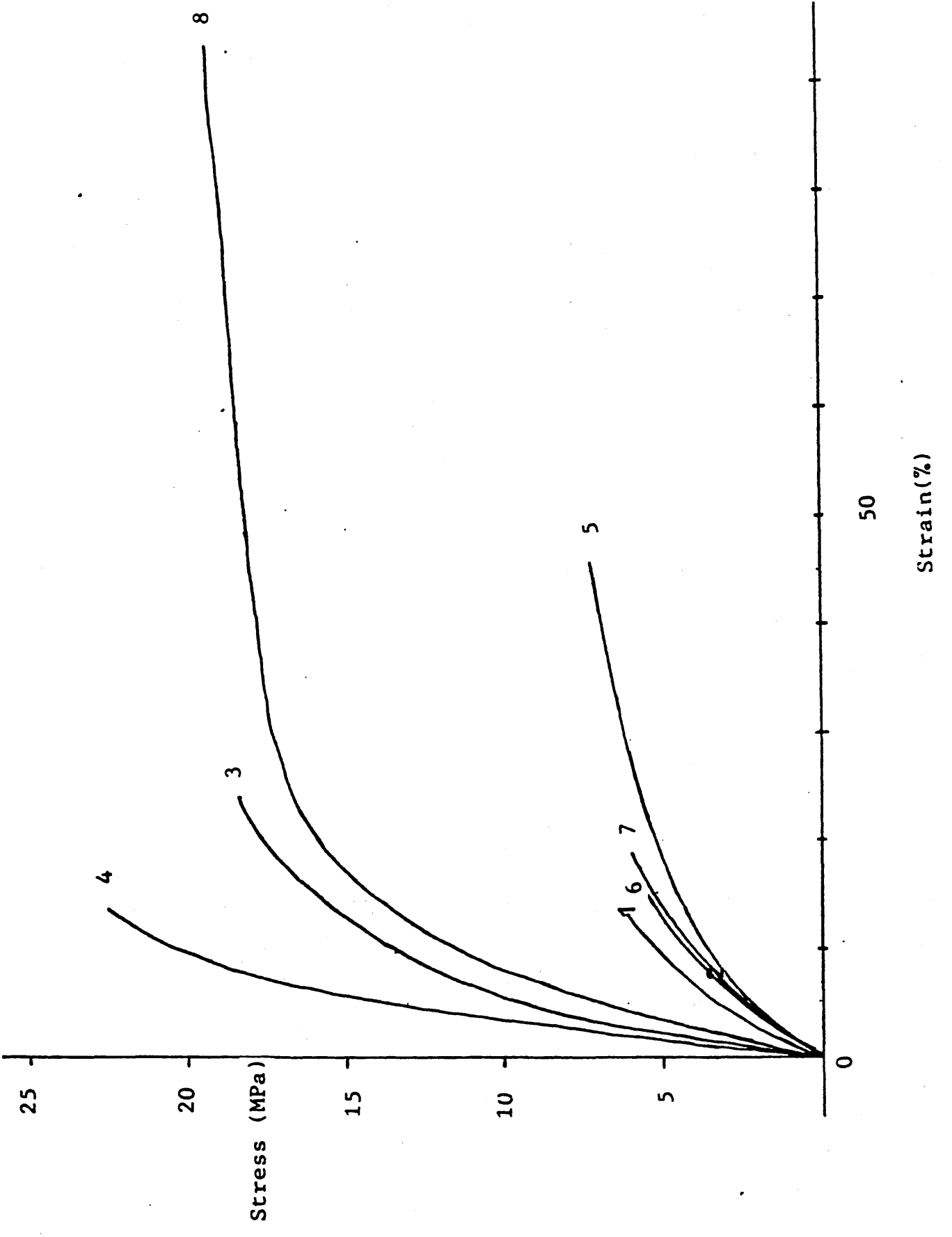


Figure 5.10 Stress- Strain Curves For PBT/PDMS Block Copolymers

Sample Index (Table 5.6)

1)	PBT - PDMS	50/50	Sn. Oct	No Vac
2)	PBT - PDMS	50/50	Sn. Oct	120 mins Vac
3)	PBT - PDMS	67/33	Sn. Oct	No Vac
4)	PBT - PDMS	67/33	Sn. Oct	90 mins Vac
5)	PBT - PDMS	33/67	Sn.Oct	90 mins Vac
6)	PBT - PDMS	50/50	DBTDL	No Vac
7)	PBT - PDMS	50/50	DBTDL	90 mins Vac
8)	PBT - PDMS	50/50	plus MDI	

It can be seen from the table that changing the composition does have a marked effect on the tensile data for the block copolymer and the following observations can be made:

(1) Changing from 50/50 m/m ratio in general improves the tensile properties of the PBT - PDMS copolymers.

(2) No leaching of siloxane is observed in the samples which experienced a polycondensation period. However, there is a significant decrease in elongation for the 67/33 m/m PBT - PDMS copolymer which underwent the vacuum period.

(3) The vacuum period for the 33/67 m/m ratio PBT - PDMS copolymer significantly increase the elongation of the copolymer. The product without a polycondensation period displayed such poor mechanical properties that tensile tests proved impossible.

The side reaction of siloxane condensation occurs in both compositions and this is reflected in the data. For the 67/33 ratio the decrease in elongation after

polycondensation is most likely due to this. However, condensation proves beneficial in the higher siloxane ratio composition. This is probably because a high RMM siloxane polymer is being formed, containing small segments of PBT along the backbone which act as reinforcement sites.

From the results it appears that a 50/50 m/m ratio for copolymer formation is not the optimum ratio when using stannous octoate as the catalyst. However, although there is an increase in tensile properties when altering composition, this is not significant enough for them to be considered as effective toughening agents, as the copolymers are still relatively weak.

5.35 Effect of Catalyst on Mechanical Properties of PBT - PDMS Copolymers

A number of catalysts were investigated as ways of optimising the copolymer formation and hence improve its mechanical properties. Stannous octoate, due to tis ability to catalyse the siloxane condensation, could not be utilised. Both tetrabutyltitanate and Ni (II) acetate did not prove suitable for the formation of low RMM copolymers. Di butyl tin dilaurate (DBTDL) was effective in forming low molar mass copolymers.

However, tensile data (Table 5.6, Figure 5.10) for the DBTDL catalysed copolymers (sample no. 6,7) are not very encouraging. The copolymer with a polycondensation period exhibits tensile properties very similar to the stannous

octoate catalysed copolymer without a polycondensation period. For the DBTDL catalysed copolymer, which has experienced a polycondensation period, there is a slight increase in properties over the copolymer without a polycondensation period, but this is not particularly significant. No leaching of siloxane occurs using DBTDL as catalyst and therefore it appears to be a less effective siloxane condensation catalyst.

5.36 Mechanical Properties of Diisocyanate Coupled PBT - PDMS Copolymers

As discussed in Chapter 4, the addition of a diisocyanate to the low RMM copolymer produced a noticeable increase in viscosity. On inspection after cooling, a mechanically very promising material was found. Tensile data (Table 5.6, Figure 5.10, sample no. 8) confirmed this showing a 4 - 5 fold increase in elongation over previous PBT - PDMS copolymers.

The stress strain curve can be divided into two main regions. In the first region (up to about 25% elongation) the hard crystalline matrix is deformed. The original crystalline matrix is progressively disrupted until at about 25% elongation it has completely disintegrated.

The second region between 25% and 100% elongation, shows yielding of the polymer due to orientation and rearrangement of crystallites under the influence of shearing forces. This is followed by stress being transmitted through the soft segments up to the point of rupture at their maximum extension.

The improvement in mechanical properties can be attributed to some extent to partial differences in the degree and nature of the crosslinks. The crosslinking in PBT - PDMS copolymers is exclusively of a physical nature as a result of the presence of interconnected PBT crystals serving as tie points. The PBT - PDMS copolymers, using an excess of diisocyanate as a coupling agent, contain additional chemical tie points formed by allophanate structures. These extra chemical crosslinks lead to a more uniform stress distribution throughout the sample, thus preventing plastic flow of the strongest PBT crystals.

However, the main improvement in mechanical properties can be assigned to the increase in the RMM diisocyanate extended copolymer affords.

5.37 Tensile Studies of PBT/ Block Copolymer/ PDMS Blends

Although initial results utilising the PBT - PDMS copolymer as a rubber toughening agent in a PBT matrix had been disappointing (section 5.32), the route was investigated further. However, this time melt blending was performed

using the Brabender plastograph. The amount of copolymer was increased to 10% by weight and it was used as a toughening agent alone as well as in conjuction with high molar mass PDMS. The reason for this was that the copolymer itself may not be effective enough to act as a toughening agent. However in conjunction with siloxane rubber, it may act as a compatibilising agent between the two separate phases. The copolymer prepared at a 50/50 m/m ratio using stannous octoate as the catalyst was used.

The results of the tensile experiment are reported in Table 5.7 and Figure 5.11.

TABLE 5.7 Tensile Data of PBT/Block Copolymer/PDMS Blends

Sample	Tensile Strength/MPa	Elongation at break %	Youngs Modulus / MPa	Area to End /J
9	32.7	5.29	960	0.178
10	38.82	11.36	1000	0.511
11	36.25	23.67	1051	1.17
12	37.42	17.55	1096	0.843
13	22.78	8.44	792	0.244
14	26.44	7.152	873	0.221
15	6.41	13.98	64	0.078
16	56.1	27.7	1980	1.20

Highest three results averaged

Strain rate = 6mm min^{-1}

PDMS from J - Sil Silicones
M_n = 450,000 - manufacturers spec.

Sample Index (Table 5.7)

9) PBT + 20% BCP (PBT - PDMS 50/50 m/m)

10) PBT + 20% BCP + Irgafos 168

11) PBT + 8.33% PDMS + 3.33% BCP

12) PBT + 10% PDMS

13) PBT + 16.7% PDMS + 6.7% BCP

14) PBT + 20% PDMS

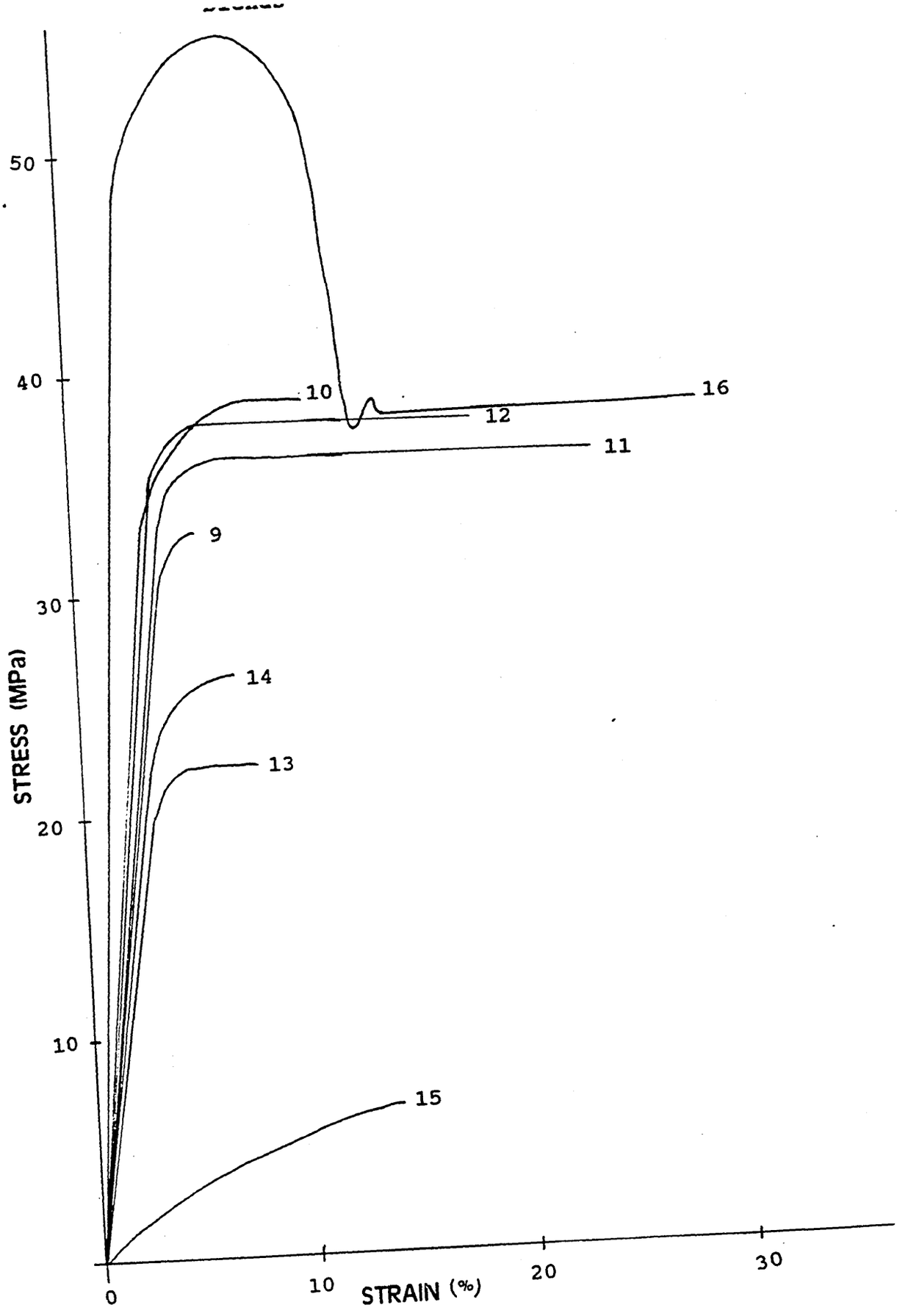
15) BCP

16) PBT (ex Brabender)

Although no significant increases in mechanical properties were observed the following points were noted:

1) Addition of Irgafos 168 limited the extent of transesterification between block copolymer and matrix. Without the phosphorous compound present the ester interchange reaction between the polyester segments is not limited, leading to short segments and a loss in mechanical properties.

2) Addition of both the block copolymer and rubber to the matrix leads to mechanical properties better than just addition of rubber or just block copolymer. The copolymer itself posesses poor mechanical properties and its presence in the PBT matrix disrupts the packing of the crystals and detracts from the mechanical properties of the PBT. This occurs with high RMM PDMS rubber, but failure this time is enhanced by incompatibility of the two phases and hence lack of adhesion between the rubber particles and the


50
40
30
20
10
STRESS (MPa)
10
16
12
11
9
14
13
15
0
10
20
30
STRAIN (%)

matrix, rather than poor mechanical properties of the rubber.

The addition of both copolymer and rubber is an improvement over the other two systems since the copolymer increases interfacial adhesion between the thermoplastic matrix and siloxane rubber, giving better mechanical properties.

3) Addition of 20% rubber to the matrix gave mechanical properties which were worse than those obtained by the addition of 10% rubber. Rubber addition strongly influences the tensile behaviour of the PBT matrix and the overall effect is a decrease of the modulus and of the ultimate properties such as yield stress and elongation at break. Lowering of the modulus may be attributed to the effect of the rubber decreasing the overall crystallinity of the material. The greater the rubber content the greater the effect on the modulus.

5.38 Impact Studies of PBT/Block Copolymer/PDMS Blends

Further studies into the mechanical properties of the most promising copolymer modified blends, as interpreted from the tensile data, was performed utilising a computer interfaced impact tester.

Results of falling weight impact testing experiments are presented in Table 5.8 and Figure 5.12. The moulded sheets often contain flaws and the data in Table 5.8 represents only the strongest 50% of the samples tested. The samples

tested were PBT plus either block copolymer or PDMS rubber, with a constant 10% by weight of siloxane rubber present. In all experiments the sample was fractured.

TABLE 5.8 Impact Data of PBT/Block Copolymer/PDMS Average Values

Sample	Fc(N)	Dc(mm)	Ec(J)	Ef(J)	Ec/Ef
PBT(ex brabender)	386	5.8	0.72	1.35	0.54
PBT + 10% PDMS	375	4.8	0.74	1.20	0.62
PBT + 20% BCP	182	5.5	0.29	0.46	0.65
PBT + 8.33% PDMS + 3.33% BCP	679	6.5	1.71	2.46	0.68

All measurements were carried out at $20^{o}C \pm 1^{o}C$

Velocity 3.0 ms^{-1}

Fc = force at cursor (maximum force)
Dc = displacement to maximum force
Ec = energy to maximum force
Ef = energy to failure

The following observations can be made:

(1) For most samples the reproducibility was not very good, but the average values are in agreement with the strongest values.

(2) PBT plus block copolymer is weaker than PBT, while PBT plus rubber is similar to PBT.

(3) PBT plus copolymer and rubber exhibits the best impact properties showing an improvement over PBT.

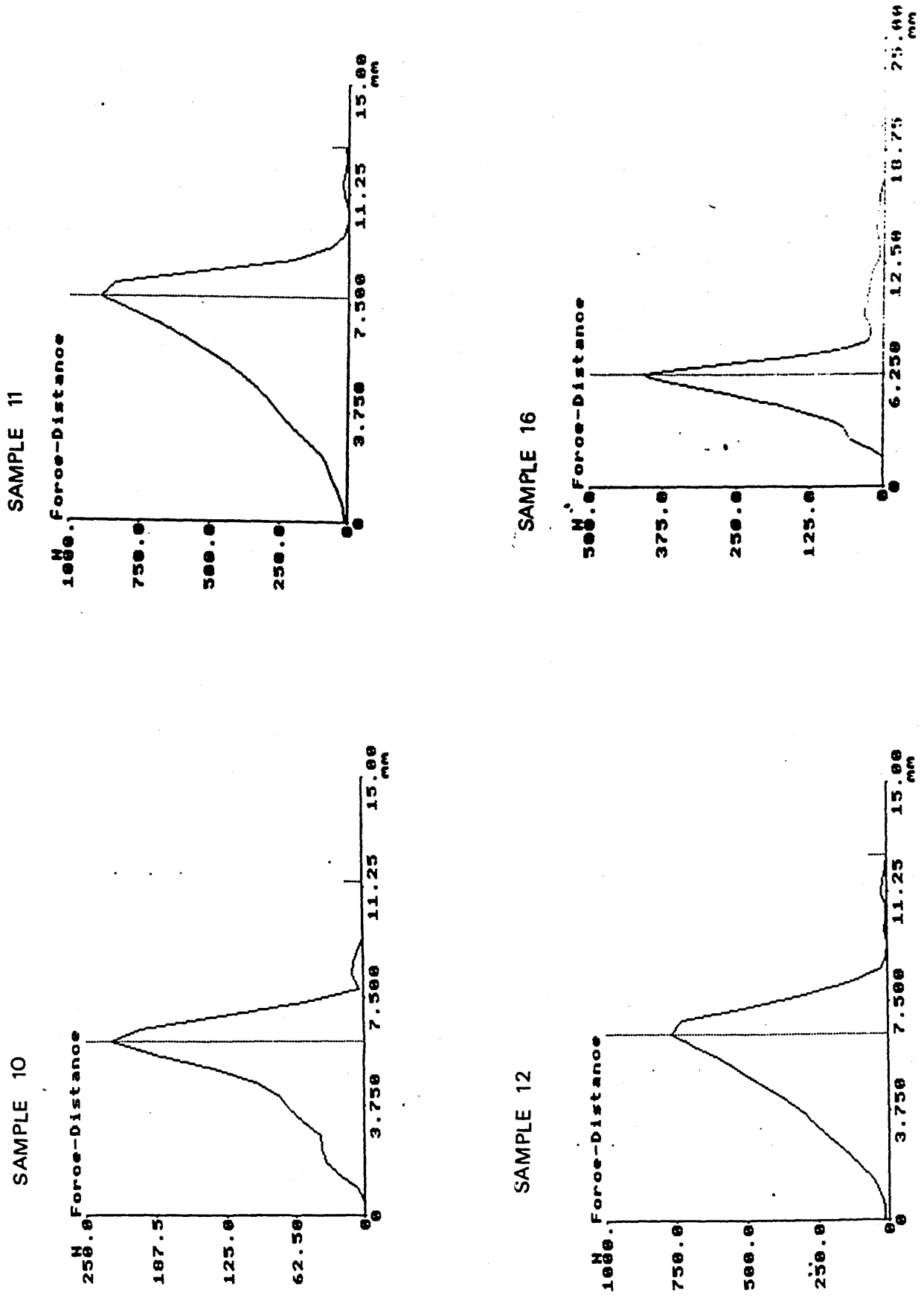


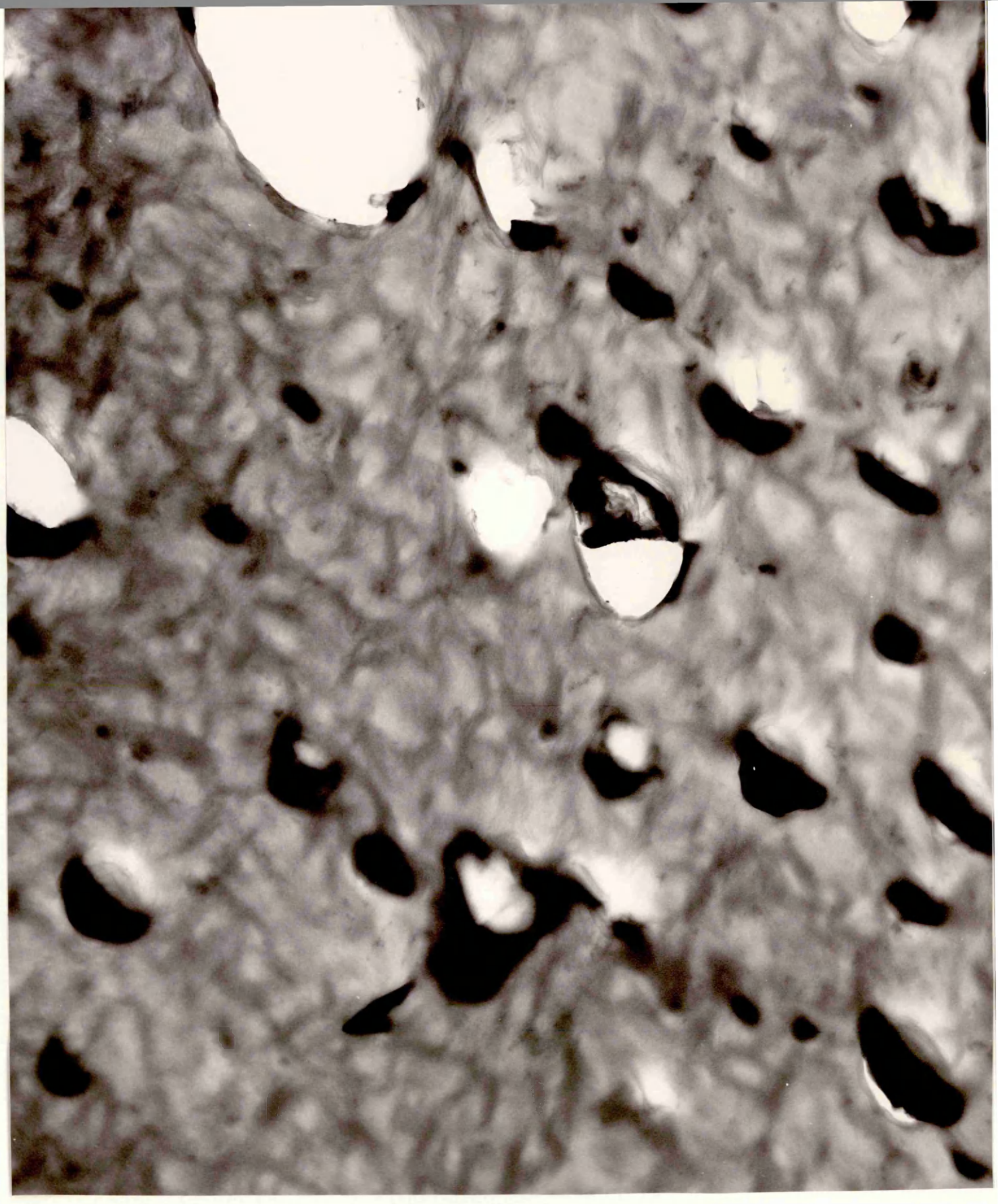
Figure 5.12 Typical Force-Displacement Curves For PBT/Copolymer/PDMS Blends

The impact data are in agreement with previous tensile data obtained for these blends. PBT plus copolymer and rubber was the most promising. It would appear that the presence of the copolymer acts as a compatibilizer generating interfacial adhesion between the rubber and PBT matrix and is reflected in the improved impact properties.

5.39 TEM Studies of PBT/Block Copolymer/PDMS Blends

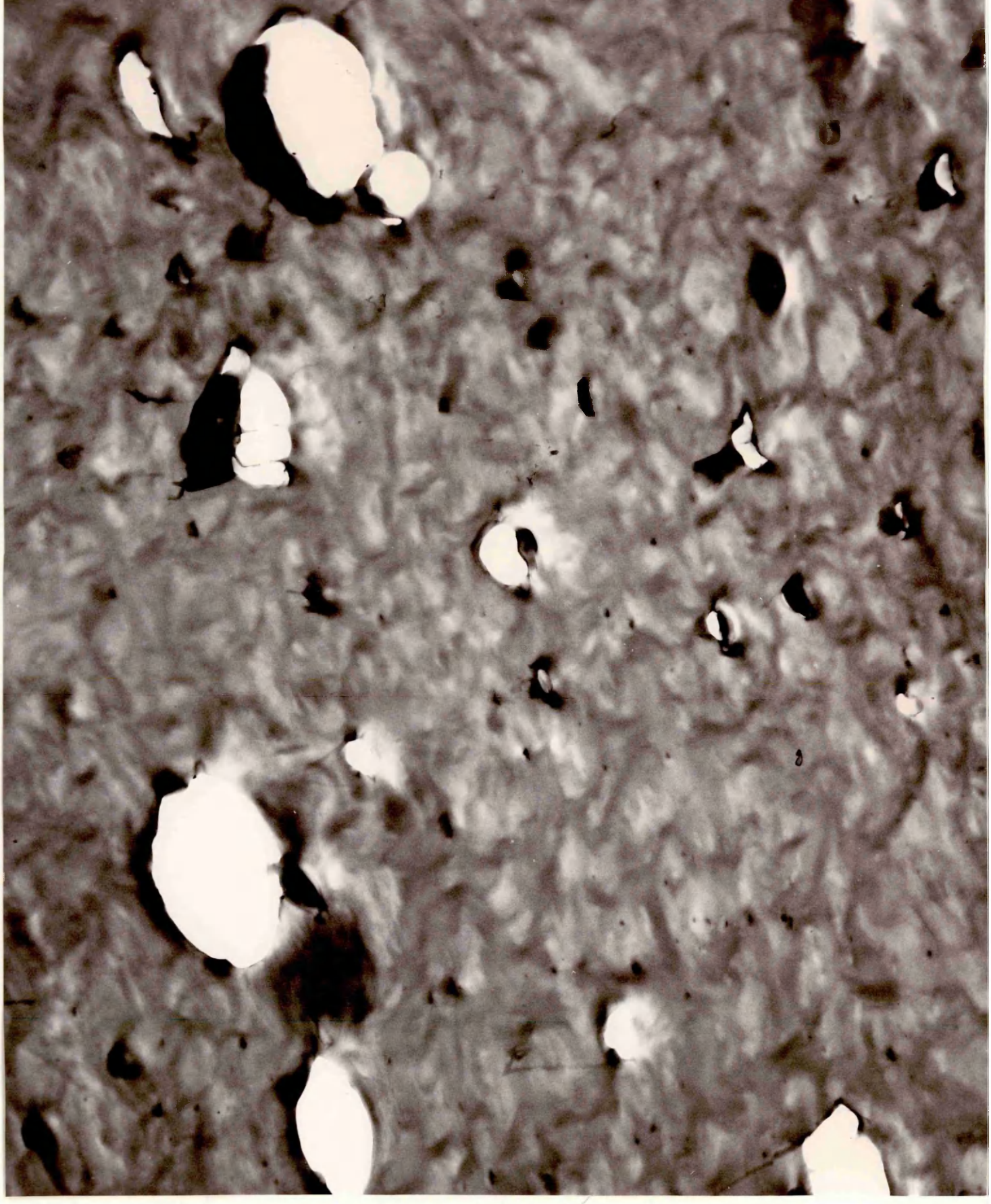
TEM micrographs of the three different PBT/Block Copolymer /PDMS blends (sample No's 10 - 12) show a variety of morphologies. The TEM micrograph of PBT blended with 10% by weight of high RMM PDMS (sample No 12 micrographs 11, 12) exhibits spherical like domains of the minor component dispersed in a matrix of the major component. The rubber particles vary in size but are predominantly in the range of 1-6μm in diameter. A number of particles are therefore of the optimum size to initiate crazes in the matrix. However relatively circular holes are present in the micrographs where the rubber phase has fallen out, before taking up much strain. This indicates poor interfacial adhesion between the matrix and rubber and effectively limits the extent of toughening.

The TEM micrograph of the PBT matrix blended with copolymer alone (sample No. 10 micrograph 13) shows a rippled effect, which was initially assigned to the fact that the material is highly stressed and difficult to microtome. However similar rippled effects have been noted by Flexman (271),



Micrograph 11 PBT Blended With 10% High RMM PDMS

Magnification x 10000



Micrograph 12 PBT Blended With 10% High RMM PDMS

Magnification x 10000

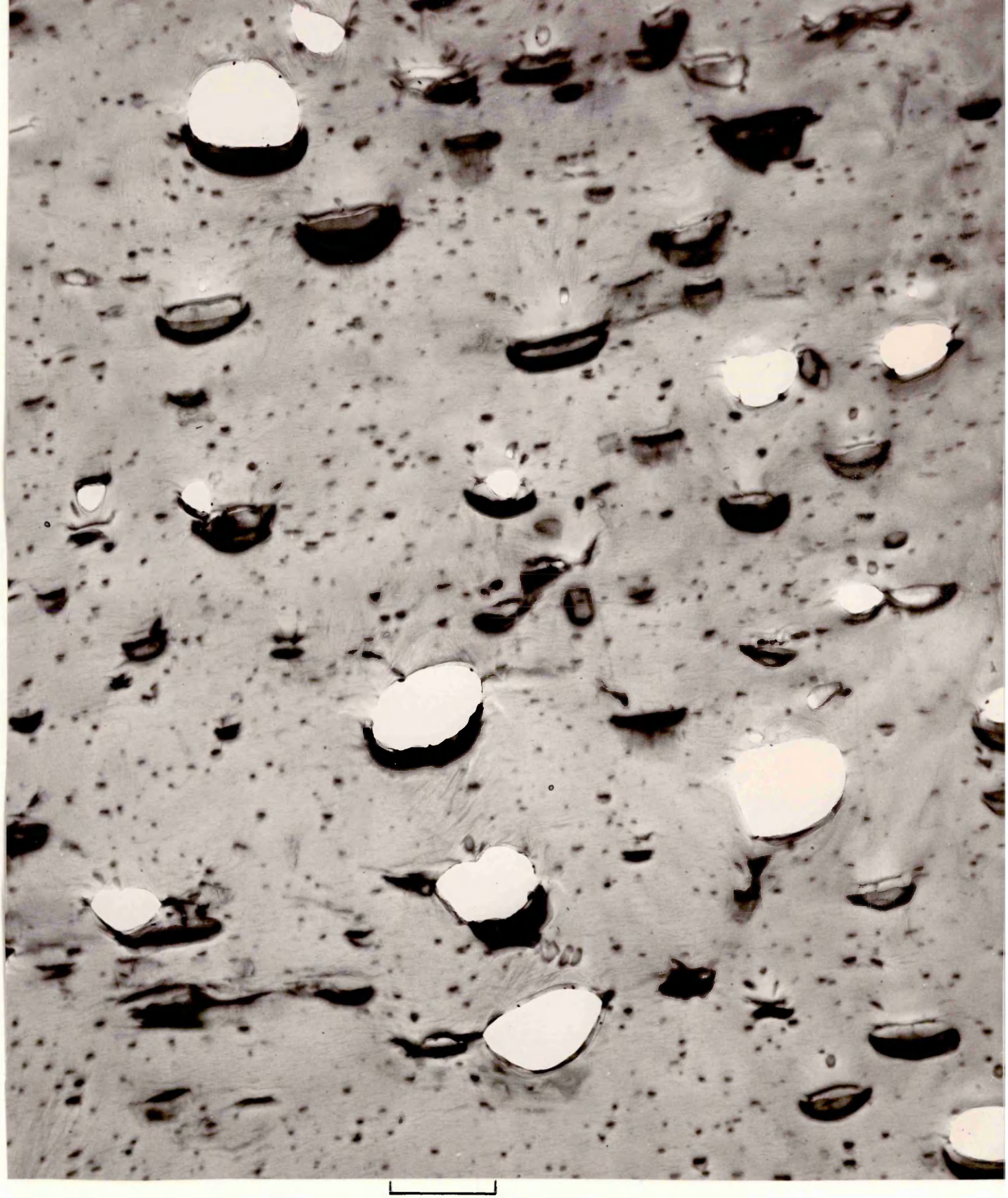
Hahn et al (272,273) and Speroni et al (274) in toughened polyamides. The latter interpreted this as an effect of a shear mechanism associated with extensive cavitation. Cavitation initiated by rubber particles has been observed previously in semi crystalline polymers. Ramsteiner and Heckmann (275) and Borggreve et al (31) observed it in toughened nylons and Polato (276) in toughened PBT. In our PBT/copolymer blend the particle size (0.1-1μm) of the rubber domains is of that where a shear yielding mechanism would be operative. However from micrograph 13 it is impossible to say whether shear yielding together with cavitation has occurred.

The smaller size of the dispersed phase in the PBT/copolymer blend, as compared with PBT/PDMS blend, is due to the difference in RMM. The high RMM siloxane forms larger rubber domains than the relatively low RMM copolymer under the same processing conditions. The small particle size for the copolymer blend is too small to toughen the matrix and this is reflected in both the impact and tensile data.

The micrograph of the PBT/copolymer /PDMS blend (sample No. 11, micrograph 14) shows that the rubber particles are smaller than when the siloxane is blended with only the PBT matrix. A spherical particle size of maximum diameter 2.5μm exists now. The addition of the block copolymer has lead to a finer dispersion of the rubber phase. The

Micrograph 13 PBT Blended With 20% PBT-PDMS Block Copolymer

Magnification x 10000



Micrograph 14 PBT Blended With 8.33% PDMS

And 3.33% PBT-PDMS 50/50 m/m Copolymer

Magnification x 10000

particle size is more conducive to initiate and blunt crazes. Moreover, there are now more rubber particles in their sites than have been removed.

These observations suggest that the block copolymer has acted as a compatibilising agent and increased the interfacial adhesion. This is evident from the fact that the rubber particles in situ are quite highly strained. The holes left by poorly adhering particles, possibly unstabilised high RMM PDMS, show little strain. The small particles may be of excess block copolymer. The reasons for this belief lie in the fact that the particle size is similar to that in the PBT/block copolymer blend. The PBT/block copolymer/PDMS gave by far the best toughening results.

6. SUMMARY AND SUGGESTIONS FOR FUTURE WORK

6.1 Summary.

A number of α, ω functionally terminated siloxane oligomers of different RMM have been synthesised and characterised to some extent. α, ω hydride terminated PDMS was synthesised by the acid catalysed redistribution reaction of octamethylcyclotetrasiloxane (D_4) and 1,1,3,3 - tetramethyldisiloxane. An important copolymer component, this proved to be a useful precursor to other functionalised siloxanes. Carboxydecyl - and glycidoxypropyl terminated siloxanes were derived from this via hydrosilation reactions.

However, carboxyl groups can react with Si - H groups to form silylated derivatives. Therefore in preparation of the carboxy functionalised siloxanes, protection of the carboxylic acid group was necessary using trimethylchlorosilane as the protecting species. The trimethylsilyl group can be easily removed by boiling alcohol. This eliminates any problems of further siloxane redistribution reactions which may have been the case if the protecting group had required an acid or base to deprotect.

Primary amine functionalised siloxanes were considered an important copolymer precursor and have been used in several situations (76). Trimethylsilyl protected allylamine though proved ineffective in functionalising hydride terminated siloxane via hexachloroplatinic acid catalysed

hydrosilation. Poisoning of the catalyst was suggested as a possible reason for the incomplete functionalisation, but further work is needed to comfirm this.

Other functionalised siloxanes of interest were obtained from commercial sources. α,ω carboxypropyl-, hydroxypropyl -,aminopropyl - , glycidylpropyl were all potential copolymer precursors and available in suitable oligomeric RMM. An advantage of all these materials was the preformed Si - C bond. This is favoured in siloxane containing copolymers for its superior hydrolytic stability compared with the Si - O - C link, and a main objective of this work was to form copolymers containing the Si - C link.

A number of α, ω hydroxy PBT oligomers were prepared, characterised and supplied by Akzo. A small scale laboratory experiment was performed using a stoichiometric imbalance of reactants to prepare low molar mass polyesters.

Experiments were performed to functionalise PBT with vinyl end groups, in order to form mutually reactive oligomers with hydride terminated siloxanes. Initial reactions concentrated on using acryloyl chloride and acrylic acid in solvent. Chlorobenzene and a N - methyl pyrrolidone/toluene mixture were used as PBT is not soluble in common inexpensive solvents. Partial functionalisation occurred with acryloyl chloride.

Owing to the limited success of the solution route, melt functionalisation of PBT was investigated. 10 - undecenoic acid and 10 - undecenoyl chloride were used as the vinyl end group source because their higher boiling points enabled them to take place in melt reactions at 240°C. Successful functionalisation and high rates of conversion were obtained in all cases. A number of catalytic species were investigated to optimise the esterification reaction between undecenoic acid and PBT. The greatest conversion of hydroxyl groups was achieved in the p - toluene sulphonic acid catalysed reaction. However, an accompanying isomerisation of the vinyl end groups excluded this route. Tetrabutyltitanate (remaining in the PBT following polymerisation) and stannous octoate were also investigated as catalytic species. However, these gave no additional benefit in the conversion of hydroxyl groups as compared with a system in which no specific catalyst was used. The use of a vacuum period did increase the conversion of hydroxyl groups but occurred with a concurrent increase in the RMM of the polyester due to polycondensation reactions.

The route chosen to functionalise PBT oligomers with terminal vinyl groups, was a melt reaction between α, ω hydroxy PBT and undecenoic acid at 240°C, in which the titanate present in the PBT had been deactivated with a phosphorous compound. A short vacuum period (<10 mins) was used at the end of the reaction.

Initial PBT - PDMS copolymer synthesis concentrated on the chloroplatinic acid catalysed hydrosilation of vinyl terminated PBT and hydride terminated siloxane in solution. Initial investigations concentrated on a common solvent, since the difference in Hildebrand solubility parameters of the two polymers is great and their respective solvents differ greatly. Chlorobenzene and dichlorobenzene were evaluated as possible solvents. PBT showed some affinity for chlorobenzene and dichlorobenzene at temperatures approaching their respective boiling points. However copolymer formation was unsuccessful.

Limited copolymer formation was observed when a blended solvent of tetrachloroethane/nitrobenzene was used. However, a competing reaction (the self condensation of Si - H functional groups,) and is accelerated by the presence of tetrachloroethane, prevents use of this route. The use of high boiling solvents added to compatabilise the reaction medium proved unsuccessful.

In view of the lack of success with solvent reactions an investigation into block copolymer synthesis by melt techniques was initiated. The hydrosilation reaction was explored using hexachloroplatinic acid as catalyst. Initial reaction products were grey in colour which was attributed to a fine dispersion of platinum metal. This had arisen as an aged catalyst solution had been used in which the Pt (IV) species had been reduced to Pt (II). On reaction with the Si-H groups further reduction occurs

resulting in Pt metal. Melt hydrosilation reaction products using freshly prepared calalyst solution also showed grey colouration when the reaction time was greater than one hour. This was due to long term thermal instability of the hexachloroplatinic acid at 240°C. Other potential hydrosilation catalysts investigated proved to be thermally unstable at melt reaction temperatures, or if thermally stable proved to be ineffective catalysts. Under the solution and melt reaction conditions investigated the hydrosilation route proved to be not viable for PBT - PDMS copolymer formation.

Owing to the difficulties involved in establishing a common solvent, all other routes investigated for the formation of a PBT - PDMS copolymer were performed in the melt phase. The esterification reaction between carboxydecyl - PDMS and α, ω hydroxy PBT and subsequently lower RMM carboxypropyl - PDMS proved unsuccessful. Incompatability problems were experienced in both cases, resulting in little reaction between the mutually reactive end groups.

A transesterification melt synthesis was successful for the formation of a segmented PBT - PDMS copolymer. This was formed with a 50/50 mass/mass ratio of α, ω hydroxy PBT (RMM 2000) and α, ω hydroxy propyl PDMS (RMM 1,000) catalysed by stannous octoate. The level of incompatability between these two polymers is demonstrated by increasing the RMM of the siloxane precursor to 2,000. An incompatible mixture is formed under the same reaction conditions and hence no copolymer results. However if the RMM of the PBT precursor is altered, a similar incompatability increase is not observed. In all cases when the RMM of the PBT oligomer was increased from 2,000 to 6,000 , a copolymer was formed.

The segmented copolymer formed initially is of relatively low RMM. The application of a polycondenisation reaction period rather than increasing the RMM of the copolymer (expected to lead to improved mechanical properties) unfortunately caused deterioration of mechanical properties. This was due to a competing side reaction of condensation of the siloxane diols which results in the formation of siloxane homopolymer during the condensation period. This detracts significantly from the copolymer properties. The condensation reaction is catalysed by stannous octoate, which makes this inappropriate for high RMM copolymer formation at the 50/50 m/m ratio.

Tetrabutyltitanate, extensively used as the catalytic species in the synthesis of PBT, proved not to catalyse the copolymer formation effectively. A stable complex between itself and the siloxane backbone was suggested, preventing it actively taking part in the transesterification catalysis. However, further investigation is required to establish this postulation. Dibutyl tin dilaurate effectively catalysed a PBT - PDMS copolymerisation at 50/50 m/m ratio, and although catalysing the siloxane diol condensation to a lesser extent, this did not lead to a significant improvement in the mechanical properties.

Copolymer species were synthesised at both 67/33 m/m PBT/PDMS ratio and 33/67 m/m ratio. Altering the copolymer ratios gave an improvement in the mechanical properties of the copolymer. A decrease in mechanical properties was observed for the 67/33 m/m PBT/PDMS copolymer synthesised with a polycondensation period, as compared to the 67/33 copolymer without such a period. This is explained by the competing siloxane diol condensation reaction product detracting from the copolymer properties. However, this same reaction proves beneficial in the converse ratio i.e. 33/67 PBT/PDMS copolymer. In this system the copolymer which has experienced the polycondensation period has significantly improved mechanical properties. This observation is explained by high RMM siloxane polymer being formed but which incorporates segments of low RMM PBT that act as hard reinforcement sites along the backbone.

A further and the most significant improvement in PBT/PDMS copolymer mechanical properties was achieved when using a diisocyanate to couple low RMM copolymer segments. The increased RMM of the copolymer species formed together with the accompanying allophanate crosslinks were responsible for the promising mechanical properties.

The mechanical properties of the blends of PBT and the low RMM PBT/PDMS (50/50 m/m) copolymer were inferior to the host material both when blended by a single screw injection moulder or a twin screw Brabender plastogragh. This reduction in properties is assigned to:

a) Poor mechanical properties of the low RMM PBT/PDMS (50/50 m/m)copolymer.

b) Poor adhesion of the copolymer to the matrix. The PBT segments are of too low RMM to provide sufficient interfacial adhesion between the rubber and matrix.

c) The particle size of rubber is too small (~0.1μm).

PBT fails by a crazing mechanism where a larger particle size (2-4 μm) is usually required for efficient craze initiation and termination.

However, when the copolymer was used in conjunction with high RMM PDMS, a two fold increase in impact properties over PBT was observed, together with a dispersion of rubber particles approaching the optimum size required for toughening. The copolymer species in this situation acts as a compatibilising agent between the rubber and matrix phase, aiding in stabilising the dispersed rubber particles

and increasing the interfacial adhesion between rubber and matrix, which results in the improved properties.

6.2 Future Work.

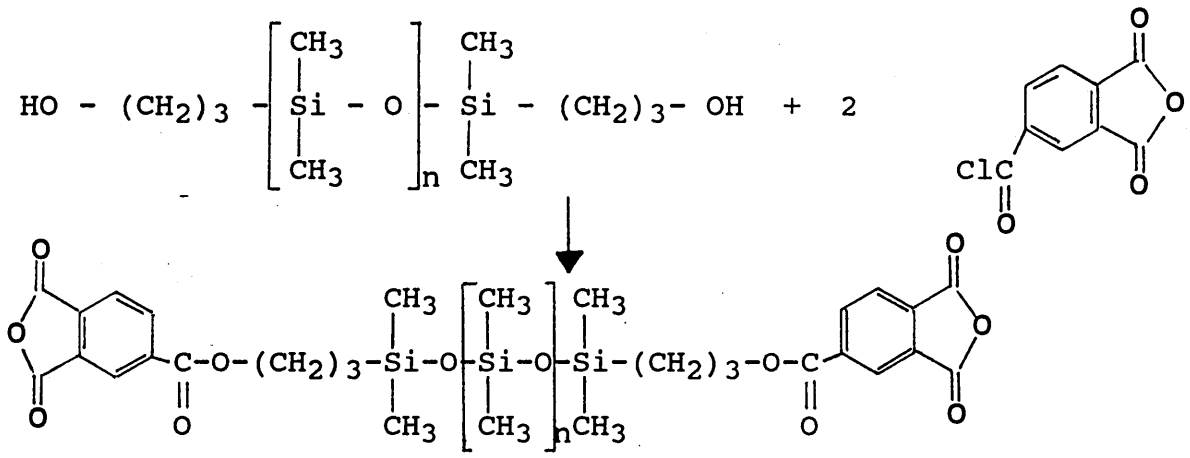
6.21 Chemical Modification

Increasing the RMM of the PBT/PDMS copolymer would be desirable. This would improve the mechanical properties, the size of the rubber particles (providing processing conditions remained constant) and probably the adhesion to the matrix.

Stannous octoate has proved to be an effective transesterification catalyst under initial copolymer synthesis conditions but is an aggressive siloxane condensation catalyst in the later polycondensation stage of the synthesis. This results in a gradual deterioration of the copolymer properties. However, metal soaps such as zinc octoate or manganese neodecanoate effectively and rapidly quench the extremely active stannous octoate (277). Therefore, once the low RMM copolymer has been initially formed, the polycondensation stage could be carried out when the stannous octoate has been deactivated. The deactivating species may prove to be an efficient polycondensation catalyst itself. A further alternative catalytic route for a copolymer formed by transesterification, would be to catalyse the reaction in two stages, as for poly(ethylene terephthalate). Firstly, the ester interchange may be catalysed by metal alkanoates e.g. acetates of zinc or manganese. Upon completion of

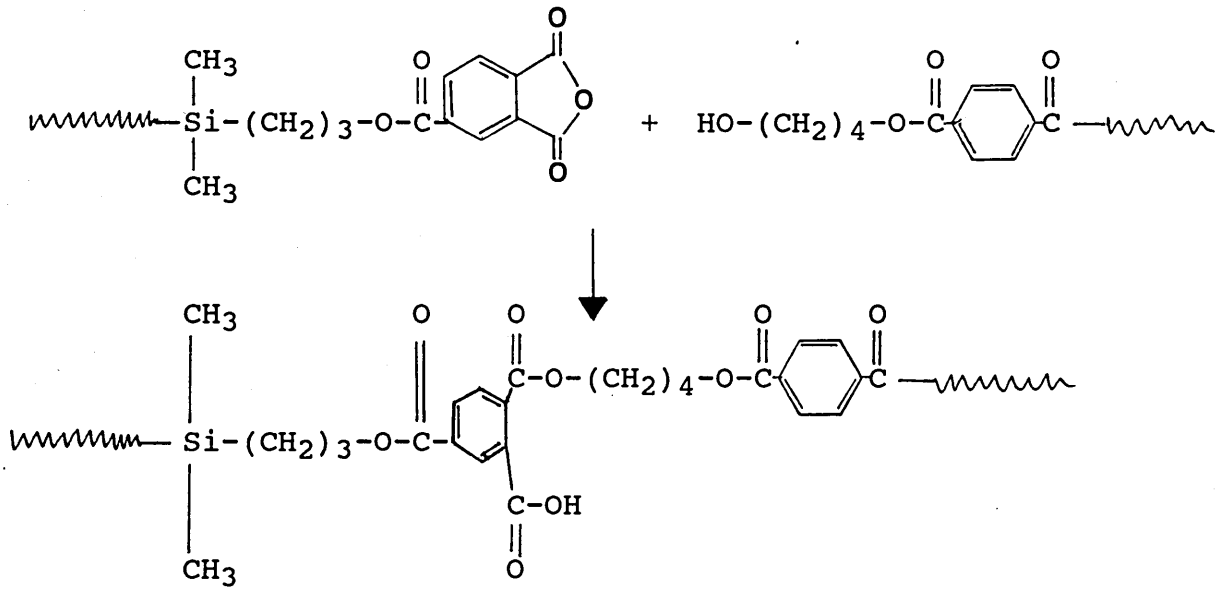
ester interchange, the first stage catalyst could be deactivated by a phosphorous compound. For the second stage, the polymerisation, an antimony compound (usually the oxide) or germanium dioxide could be investigated as catalysts.

Another alternative to avoid the competing siloxane diol condensation is to use other functionalised precursors. A possible route is to use anhydride functionalised PDMS. It has been previously demonstrated that anhydride groups grafted on to rubbers incompatible with PBT can react with hydroxide groups forming ester linkages (9,10). Therefore a proposed scheme could be the reaction of trimellitic acid anhydride acid chloride with α, ω hydroxyl propyl PDMS to produce a suitably functionalised PDMS.



Reaction Scheme 6.1 Proposed Formation of Anhydride Functionalised PDMS

The anhydride functionalised PDMS has the potential then to react in the melt with hydroxy terminated PBT as hypothesised in Reaction Scheme 6.2 below.

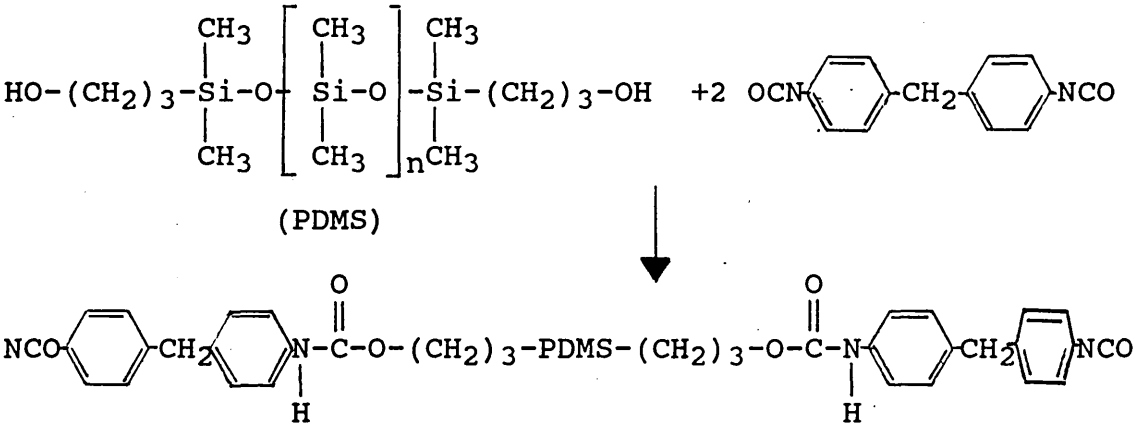


Reaction Scheme 6.2 Potential Reaction of Anhydride Terminated PDMS with α,ω Hydroxy PBT.

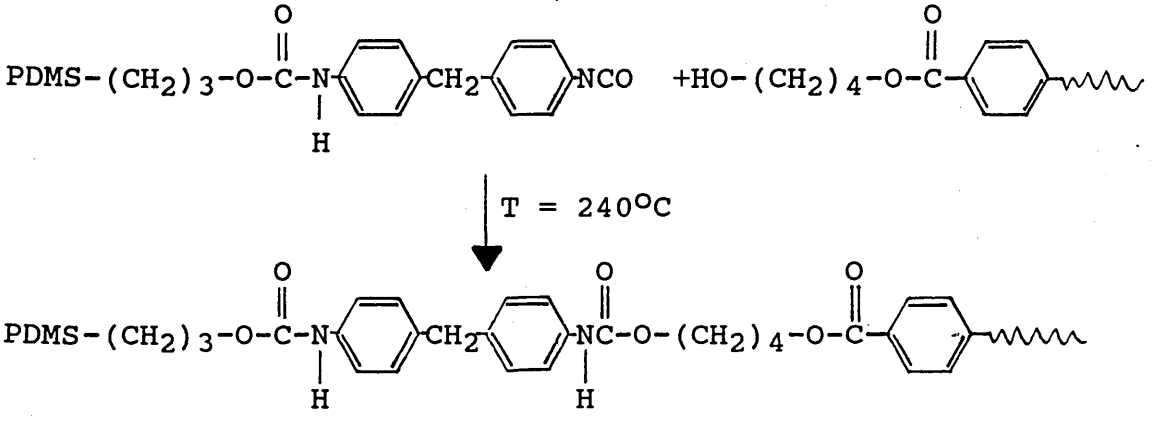
The aromatic ring attached to the PDMS precursor may aid in reducing the incompatability of the two materials, and, together with the increased reactivity the anhydride group introduces, this may prove a feasible option without the possibility of extensive side reactions. A further modification of this type of reaction is to functionalise side chain hydroxyl groups of a suitable PDMS precursor with anhydride functional groups. This could then form graft copolymers in the melt, which may also act as suitable toughening agents.

Urethane linked low RMM PBT/PDMS copolymer precursors showed a significant increase in tensile properties. A more controlled technique to achieve an alternating block copolymer, which may show an improvement upon the properties initially obtained, would be to form an isocyanate terminated PDMS precursor. This could then react further with hydroxyl terminated PBT to form a PBT/PDMS copolymer containing urethane linkages as indicated in Reaction Scheme 6.3

a) Isocyanate terminated PDMS synthesis.



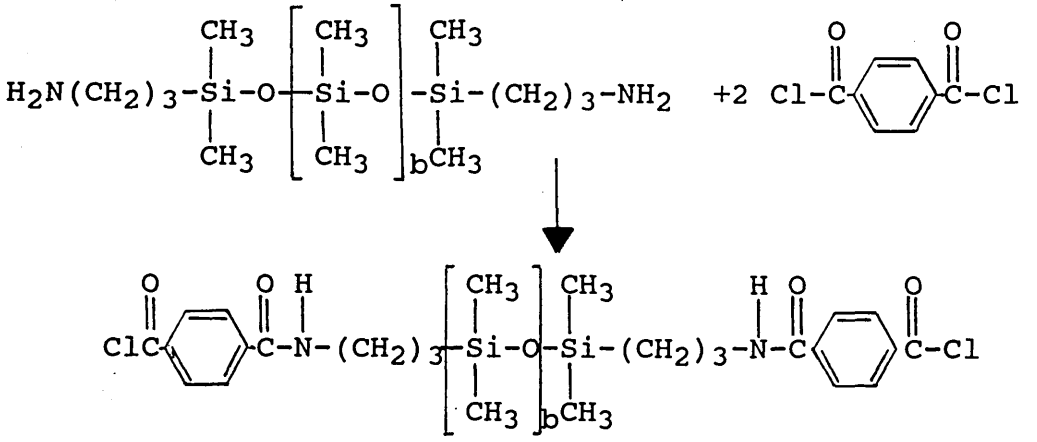
b) Copolymer Synthesis.



Reaction Scheme 6.3 Proposed PBT/PDMS Copolymer Formation Containing Urethane Linkages.

The increased reactivity of the siloxane precursor, due to the isocyanate group, should ensure reaction between itself and PBT, especially under melt conditions. As observed already in this work, the presence of the urethane linkages will enhance the mechanical properties of the copolymer. The availability of a number of isocyanates, both aromatic and aliphatic, offers final copolymers with differing mechanical properties. However, although a promising route, the health and safety issues involved with isocyanates (especially at 240^{o}C) may rule this out on a full scale operation, unless operators can be adequately protected.

Other potentially more reactive siloxanes which could be used in copolymer synthesis are hydroxyl or amine treated siloxanes which have been end capped prior to copolymer formation with either terephthaloyl chloride or isophthaloyl chloride (Reaction Scheme 6.4). Again increased compatability is expected because of the presence of the aromatic ring, and the acid chloride functionality should be more reactive towards hydroxyl terminated PBT in the melt.



Reaction Scheme 6.4 Terephthaloyl Chloride End Capped α,ω Propylamine Terminated PDMS

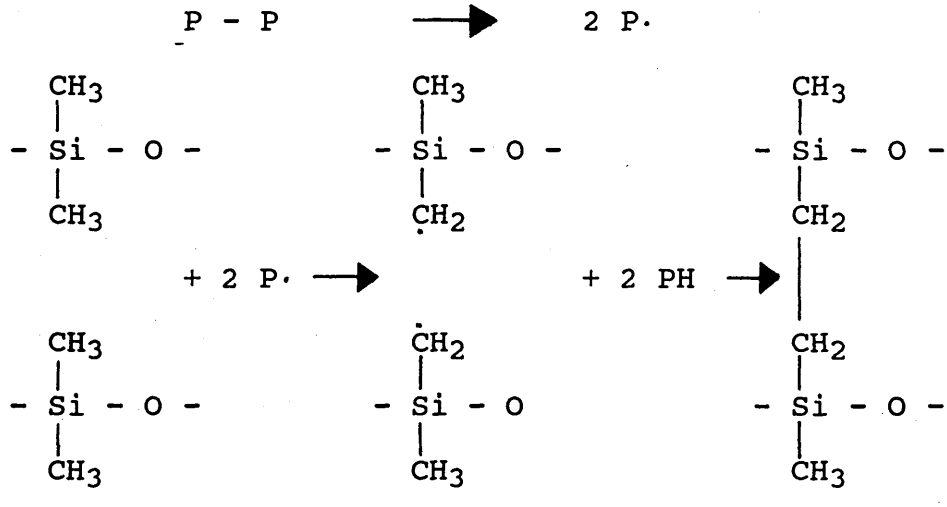
A more speculative, but very interesting, route to PBT/PDMS copolymers could be via telechelic star PDMS precursors. Amine functional star polymers have been synthesised (278) and these open up the possibility of novel star PBT/PDMS block copolymers.

6.22 Future Processing.

Of the copolymers synthesised in this work it would be interesting to measure the mechanical properties performance of PBT blended with the urethane linked PBT/PDMS copolymers and the 33/67 m/m PBT/PDMS product that has undergone a significant polycondensation period. Work should be carried out with the copolymers acting as toughening agents alone and together with high RMM PDMS, to observe their effect as compatabilising agents.

Controlled crosslinking of the rubber phase can be beneficial in rubber - toughened thermoplastics. Uncrosslinked particles tend to break down into very small particles due to intense shear and elongation stresses acting in the mixing chamber (279). During moulding the particles become highly extended and there is also the possibility of agglomeration during this stage. These tendencies lead to a reduction in mechanical strength.

Silicone rubbers can be cured with the aid of peroxides(53). The route involves the decomposition of the peroxide into free radicals, abstraction of hydrogen from the methyl group to form polymer radicals and coupling of the polymer radicals to form a crosslinked structure. The peroxide is represented by P-P and the reaction described in Reaction Scheme 6.5.



Reaction Scheme 6.5 Radical Crosslinking of PDMS.

An organic peroxide could be used in future work to crosslink the rubber phase. Effective crosslinking of PDMS particles should improve control over rubber morphology within the matrix and consequently improve mechanical properties.

Mechanical degradation occurs in PBT if suitable processing conditions are not used (9). This will be more prominent in blends of PBT and copolymer since the morphology is affected by the processing conditions too. In future work processing conditions must be optimised to produce the desired final morphology while eliminating any possibility of mechanical degradation of the host matrix.

A more speculative processing technique for copolymer formation is the use of sonochemistry. Sonication potentially provides rapid and efficient emulsification of immiscible liquids affording very large interliquid surface contact area for reaction. Therefore an ultrasonic probe placed in the melt may aid in overcoming the incompatability of the system, increase the rate of reaction and limit side reactions. However, it is uncertain whether this technique could be applied on a commercial scale.

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